STUDIES ON SOME BICYCLIC CARBANIONS

by

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C O N T E N T S

ABBREVIATIONS

Diglyme	Diethylene glycol dimethyl ether.
conc.	concentrated
M.Pt.	melting point
M,N	molar, normal
ml.	millilitre
g.	gram
tosyl	para - toluene sulphonyl
I.R.	Infra-red
U.V.	Ultra-violet
T.L.C.	Thin layer chromatography
V.P.C.	Vapour phase chromatography
mμ	millimicron
ν (cm^{-1})	frequency of absorption peak in wave numbers
s.m.w.	strong, medium, weak absorptions
λ_{max}	wavelength of absorption peak in millimicrons
N.M.R.	Nuclear Magnetic Resonance
τ	tau values for resonance maxima in N.M.R. spectrum
J (c/s)	spin-spin coupling constant in cycles per second.

SUMMARY

The aim of this work was to detect whether non-classical electron delocalization would occur between a negative charge situated at the 7-position of bicyclo (2,2,1) compounds or the 9-position of bicyclo (4,2,1) compounds and double bonds situated in other parts of systems of these types. The method chosen for detection of such interactions was comparison of the rates of removal of protons, from these positions, in bicyclic compounds with and without olefinic bonds. In order to labilize the protons at the 7- and 9-positions it was decided to synthesize compounds with phenyl substituents at these points. The key compounds required were 7-phenylnorbornadiene and 9-phenylbicyclo (4,2,1) nonatriene. The first was synthesized by a known route without difficulty and from it 7-phenylnorbornane and syn - 7 - phenylnorbornene. The synthesis of the second occupied the major part of the time available and was finally achieved by a method which was indicated, but not fully described, during the course of the work. Two earlier alternative methods failed.

The rates of exchange of the benzylic protons of 7-phenylnorbornene and cumene, used as an acyclic comparison, were measured and upper limits set on the rates of exchange of 7-phenylnorbornadiene

and syn - 7 - phenylnorbornene. At 110° the rates of exchange of the benzylic protons of 7-phenylnorbornadiene and syn - 7 - phenylnorbornene are at 1 ast 140 and 260 times respectively less than that of 7-phenylnorbornane at the same temperature. Although these rate differences are in agreement with a prediction of destabilizing non-classical interactions in compounds of this type they are not sufficiently great to prove it. An alternative explanation is that introduction of double bonds into the norbornane skeleton increases the strain energy of the molecule and decreases the stabilization of the carbanion by conjugation with the phenyl group; which would require a further increase in strain energy.

In the case of 9-phenylbicyclo (4,2,1) nonatriene it appears that treatment with highly basic medium causes several complex changes, probably involving the removal of the benzylic proton at a greater rate than that of cumene. On the basis of the strain energy argument it would be expected that the rate of removal of the benzylic proton from this compound would lie between the rates of cumene and 7-phenylnorbornane.

Further experiments in this system may yield less equivocal information than the experiments on the bicyclo (2,2,1) systems. A destabilizing interaction is predicted for anions of this type and hence reduction to the bicyclononane should cause a diminution of the rate of removal of the benzylic proton. The strain energy

argument would predict an increase in the rate of benzylic proton abstraction on hydrogenation to the bicyclononane.

CHAPTER ONE

INTRODUCTION

AROMATICITY

Early Definitions

In common use the word aromatic has a simple and precise meaning, viz. fragrant, spicy,[1] and at the beginning of the nineteenth century its meaning to chemists was the same. Since then it has acquired many other meanings and implications and the criteria for its use are now far beyond the appreciation of the human nose.

The first step from the original meaning was taken when it was realized that the majority of the fragrant compounds had chemical properties which differed markedly from those of the fatty (aliphatic) compounds. Although their molecular formulae indicated a high degree of unsaturation aromatic compounds failed to undergo addition reactions under conditions which caused aliphatic compounds to react readily. When conditions were vigorous enough to cause reaction, substitution, rather than addition, often occurred.

The recognition that these compounds contained a minimum of six carbon atoms and derived from the parent substance benzene led Kekule to propose a six membered ring structure with alternate single and double bonds for benzene[2], and led to the belief that aromatic compounds were compounds which contained such ring systems appropriately substituted, or fused, as in naphthalene.

The concept of the aromatic nucleus also led to the appreciation of further peculiarities of aromatic reactivity, such as the modifying effect of the aromatic ring on the reactivity of its substituents and of the substituents on the aromatic nucleus, both overall, as shown by rates of reaction, and selectively, as shown by wide variations in the rates of reaction at different ring positions.

In due course it was also realised that some physical properties are characteristic of aromatic compounds. High diamagnetism has been recognised for some time as indicative of aromatic character and this criterion has recently been put on a quantitative basis.[3] It also forms the basis of one of the criteria of aromaticity now in very frequent use; proton magnetic resonance shifts, as will be discussed later.

Although many compounds exhibiting the chemical and physical properties then associated with aromaticity contained rings of six carbon atoms, some had six atom rings containing heteroatoms, as e.g. pyridine, and some did not even have six atom rings, as e.g. thiophene. Nor could all examples be covered by increasing the number of nuclei considered aromatic since pyrrole exhibits some aromatic properties which it loses on protonation even though the nucleus suffers no skeletal rearrangement. These facts were rationalized by Robinson's introduction of the concept of the aromatic sextet;[4] namely that aromatic character depended

upon the presence of a cyclic system of six π-electrons.

The characterization of aromatic compounds by electronic types rather than geometric types first suggested that ions might exhibit aromatic properties and extended the use of the term aromatic to this completely new field. The parent ions suggested as aromatic by the sextet rule were the cyclopentadienide anion $C_5H_5^-$, explaining the exceptionally high acidity of cyclopentadiene which had long been known[5], and the cycloheptatrienyl cation $C_7H_7^+$[4]. The modification of the normal properties of the carbonium ions and the carbanions derived from these parents has been observed in many substances both ionic and zwitterionic.

A striking example in the cyclopentadienide anion series is provided by the remarkable chemical stability of dicyclopentadienyl iron (ferrocene[6]). An example of the increased insight given is the realization that the cycloheptatrienyl cation had been prepared as long ago as 1891 by Merling[7] (confirmed by Doering and Knox, 1954[8]).

Huckel Molecular Orbital Theory

Once aromaticity had been associated with electronic rather than skeletal structure major advances in the systems regarded as aromatic, their means of recognition, and the underlying reasons for the special nature of aromatic reactivity became possible. They were brought about by the approximations introduced by Huckel in the solution of the Schrodinger equation for polyelectronic

molecules[9] (Huckel Molecular Orbital Theory) and their later application to conjugated cyclic systems[10]. The principal rule adduced by Huckel has been stated as follows: "those monocyclic coplanar systems of trigonally hybridized atoms which contain $4n + 2$ π-electrons will possess relative electronic stability"[11].

Since, as has been seen, the term aromatic had by this time become attached to compounds containing six π-electrons, a constituent group of the $4n + 2$ π-electron series, and relative electronic stability explained the most obvious characteristic of the compounds considered aromatic, viz., their diminished reactivity, this rule has since provided the principal definition of aromatic character. The definition is imprecise in that the degree of stabilization required for the use of the term aromatic and the choice of reference compounds, in which electronic stabilization does not occur, for comparison, are both matters of opinion. In spite of this the convenience of the term, aromatic, as chemical shorthand and its long use in discussions of the properties of molecules make its understanding, with all its shades of meaning, essential, and its use almost unavoidable.

Development of Criteria for Aromaticity

The thermodynamic criterion now forms the basis for the understanding and definition of aromaticity but it is seldom used because of the labour involved in determining heats of formation of compounds and the ambiguity of the results obtained. The difference in the heats of combustion, from which heats of formation are usually calculated, of similar compounds in which electron delocalization may or may not take place is invariably small compared to the heats of combustion themselves, e.g. for benzene 30-40 Kcals in about 1000 Kcals., and hence imprecise. Also, some systems whose study is necessary are either not stable enough or not available in sufficient quantity to permit the necessary thermodynamic measurements to be made.

Some of these difficulties may be minimized by changes in technique. An example is Kistiakowsky's assessment of the resonance energy of benzene[12] by comparison of the heats of hydrogenation of appropriate compounds. These are much smaller than the heats of combustion and hence the inaccuracy in the portion of the heat of formation of benzene attributed to stabilizing electron delocalization is greatly decreased. Although accuracy may be improved in this way, the difficulties in making measurements and obtaining compounds in sufficient quantities and of sufficient stability remain. It is for these reasons that many other criteria for the detection and estimation of electron delocalization have evolved.

The determination of the shapes of molecules, whether by X-ray analysis or infra-red or Raman spectroscopy, often gives a clear indication as to whether electronic delocalization takes place, since it is usually possible to decide if the molecular dimensions can be achieved by assembling atoms with the bond lengths and angles found in molecules in which no electronic delocalization takes place. The best known example is provided by benzene in which it is believed the π-electrons are completely delocalized around the ring because X-ray crystallography shows that all carbon-carbon bond lengths are the same. This form of argument has often been used. Two interesting recent examples are provided by (16) annulene and (18) annulene. X-ray crystallography shows that (16) annulene has alternate single and double bonds[13] whereas in (18) annulene only very small differences in bond distance are observed[14] leading to the belief that extensive electronic delocalization occurs in this molecule.

A criterion of aromaticity which does not derive from the Huckel Molecular Orbital predictions of thermodynamic stability for $4n + 2$ π-electron systems is provided by the observation of proton magnetic resonance shifts. However, it derives from the same ultimate source; quantum mechanical treatment of the properties of conjugated cyclic systems. The basis was provided when London[15] succeeded in explaining the high diamagnetism of benzenoid aromatic compounds by showing that the application of an external magnetic field should induce a ring

current in 4n + 2 π-electron systems which would make a negative contribution to their magnetic susceptibility. It was later shown[16] that such a diamagnetic ring current would cause considerable downfield shifts (deshielding) of protons in the molecular plane outside the ring and even larger upfield shifts (shielding) of protons inside it. A particularly striking example is provided by trans-15,16-dimethyldihydropyrene(I). The methyl protons lie within the cavity of a π-electron cloud which shows all the normal signs of aromatic delocalization. Their proton magnetic resonance occurs at 14.25 τ as compared to an expected value of about 9 τ[17]. This is an unusually large shift, more normal values observed are about half this magnitude. Since the proton magnetic resonance criterion derives from the same base and focuses attention on the same compounds as the Huckel thermodynamic predictions conformity with it is often regarded as being equally indicative of stabilizing electronic interactions.

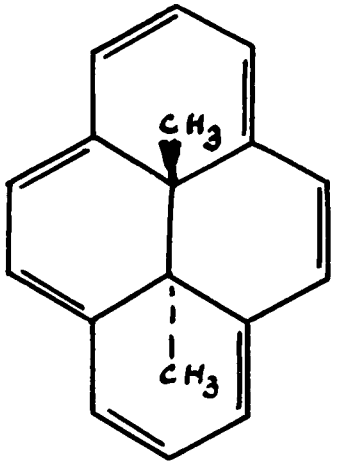
Although measurements of heats of formation of cyclic electron systems have only been carried out in a few cases other properties, both qualitative and quantitative have been taken as indications of thermodynamic properties. The simplest of these is the ease of preparation of the proposed system. Thus it has been suggested[18] that the ready preparation of the compounds contain-

ing the six π-electron cycloheptatrienyl cation system as compared with the eight π-electron cycloheptatrienide anion system is evidence of the thermodynamic stabilization predicted for the six π-electron system and not for the eight π-electron system.

The qualitative nature of reactivity, which caused the original divergence between the chemical and lay meanings of aromatic, is still in frequent use and thus the high and varied reactivity of cyclooctatetraene has also been taken as an indication that eight π-electron systems do not enjoy the thermodynamic stability of six π-electron systems. In ionic systems the rates of the processes by which the ions are formed have been taken as indications of the thermodynamic properties of the ions themselves. Much of the evidence presented in this thesis rests upon the validity of this assumption and so it will be examined in detail in the later section; Kinetic and Thermodynamic Acidities.

Developments in Planar Systems.

Since Huckel's original prediction advances have been made in the techniques of molecular orbital calculations, and more complex structures have been examined with a view to the detection of electronic delocalization. Besides calculations of the thermodynamic properties of aromatic systems, attempts have been made to predict other fundamental properties such as the nature of aromatic substitution[18] and the transmission of inductive effects[19].



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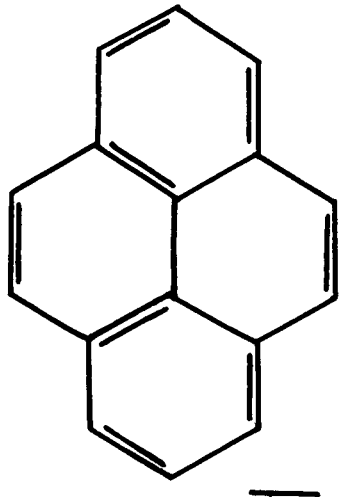

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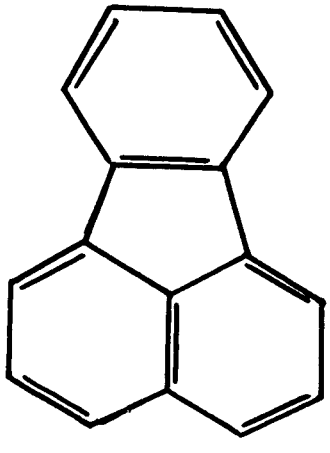
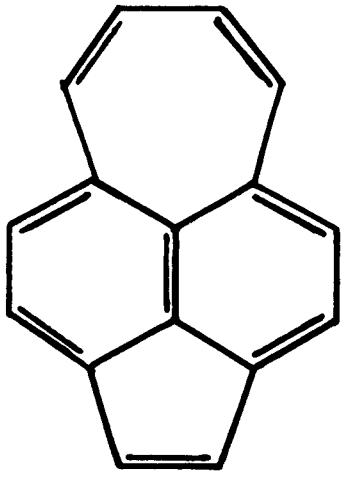


III

A great deal of experimental work has been prompted by molecular orbital predictions. The unusual stability of other members of the $4n + 2$ π-electron series such as cyclopropenium cations which are two π-electron systems[20], and cyclooctatetraene dianion[21] and cyclononatetraene anion[22], which are both ten π-electron systems have been demonstrated. The most thorough investigation into the aromaticity of unsaturated monocyclic compounds has been provided by the work of Sondheimer on annulenes[23]. Aromatic properties in these cases were inferred from effects on the various proton chemical shifts in the senses described previously and from the greater reluctance of $4n + 2$ π-electron systems as compared to $4n$ π-electron systems to undergo bending deformations of the ring which would destroy any stabilizing electronic overlap.

The series also provides a good example of the more accurate predictions which can be made by refined molecular orbital theory. Dewar has predicted[24] that the highest member of the annulene series to show aromatic properties will be (22) annulene and this has been confirmed by examination of (26) annulene which shows no aromatic properties[25]. An interesting example of aromaticity effects in anions is shown by the retention of a planar geometry (and hence electronic overlap) by the dianion of (16) annulene at 140°[26] although the parent compound is non-planar[13] and undergoes rapid conformational changes at -60°.



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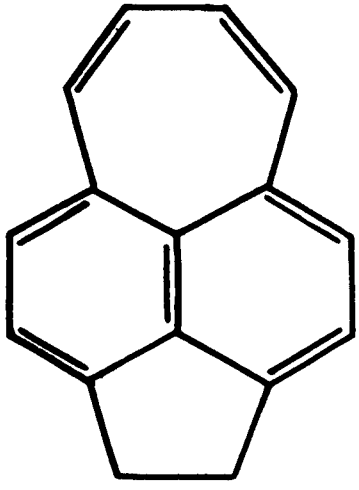

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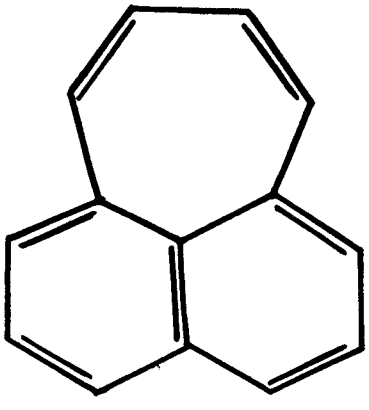


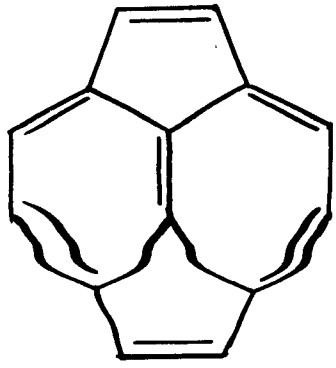
VI

The success of the 4n + 2 rule has prompted attempts to extend its application to systems which are not monocyclic and coplanar. The most obvious extension is to polycyclic systems but there are clear exceptions to its predictions, e.g., pyrene (II) and fluoranthene (III) are both stable aromatic compounds which possess 16 π-electrons. Greater success has been achieved by regarding aromatic molecules as being composed of a peripheral cyclic polyene, to which the 4n + 2 rule applies, and internal cross links which cause only a small perturbation.[27]

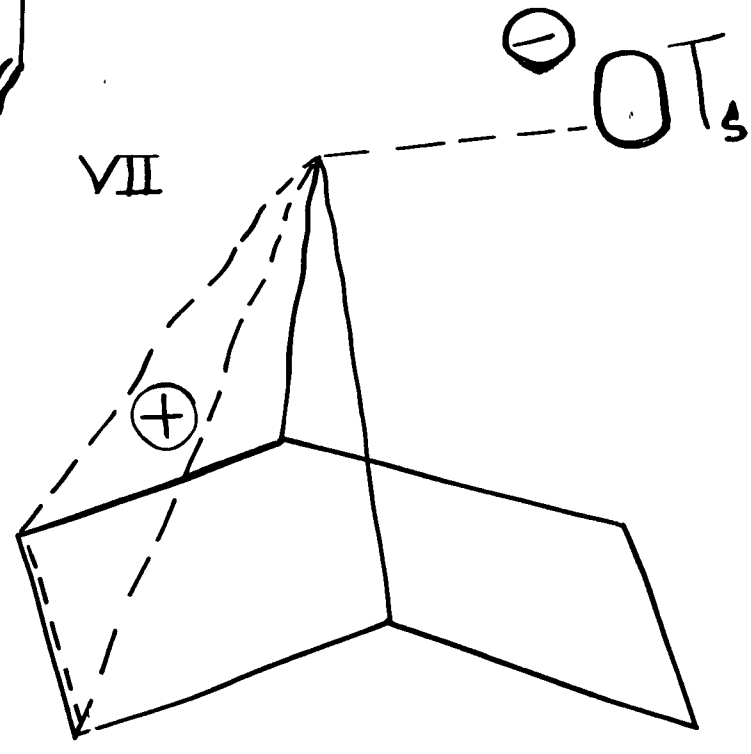
An early example, and one in which the evidence is unusually clear cut, is provided by acepleiadylene (IV) which has a 14 π-electron perimeter and will not react with maleic anhydride under conditions that produce Diels-Alder adducts with pleiadiene (V) and acepleiadiene (VI).[28] An example of more recent work is provided by pyracyclene (VII) which has a 12 π-electron perimeter and would be predicted to suffer electronic destabilization. The chemical evidence in this case is much less clear cut[29] but molecular orbital calculations have been carried out which suggest interesting alternative electronic structures for the neutral molecule itself, and for the dication and dianion which may be derived from it.[30]

Development in Non-Planar Systems

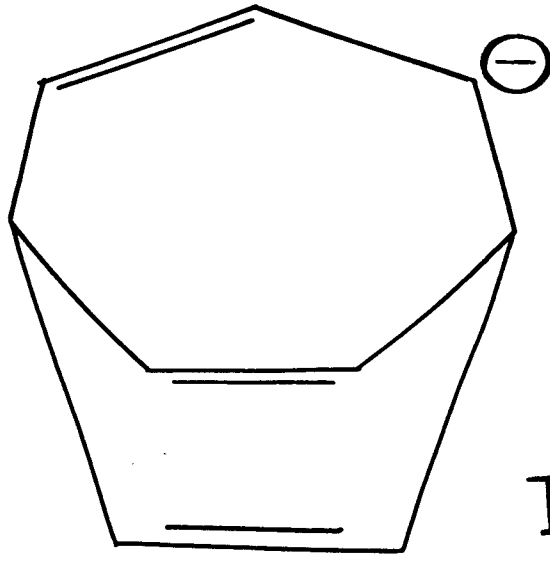
Systems in which the components between which electronic overlap is expected are not coplanar have also been examined.



VII



VIII



IX

Since this thesis is concerned with delocalization in non-planar systems only a brief outline will be given here, examples of particular relevance will be discussed later.

The earliest example involved the constituents of the cyclopropenium cation; viz., a carbonium ion and a carbon-carbon double bond; held in fixed relationship by a norbornyl ring system. The acetolysis of anti-7-norbornyl-p-toluenesulphonate proceeds 10^{11} times faster than that of the corresponding saturated compound and with complete retention of configuration,[31] a combination which strongly suggests stabilizing electronic overlap in the transition state (VIII) as observed in cyclopropenium cations. Evidence in support of this conclusion has been obtained by placing the same components in close proximity, though not in conjugation in other rigid ring systems.[32,33,34]

A further deviation from the simple Huckel rule is provided by the substitution of a cyclopropyl group for a carbon-carbon double bond as the source of two electrons. Both the earliest example[35] and the most precise evidence of the steric requirements for electron delocalization have involved cyclopropenium analogues.[36,37]

The references quoted previously all refer to electronic delocalization between two non-planar components. The possibility of simultaneous electron delocalization between three non-planar components has been suggested for some time by the heat of hydrogenation of the first double bond of bicyclo (2,2,2) octa-

2,5,7-triene (barrelene) which is the highest known for any carbon-carbon double bond.[38]

The possibility of such three centre interaction had previously been suggested in the case of norbornadienyl cation[39] on the basis of the enhanced rates of solvolysis of 7-norbornadienyl derivatives as compared to anti-7-norbornenyl derivatives. However, observation of the proton magnetic resonance spectrum of the 7-norbornadienyl cation shows that the two vinyl bridges are magnetically non-equivalent.[40] This suggests that electron delocalisation occurs between the bridgehead and only one double bond, as in the 7-norbornenyl cation. Amplification is provided by a molecular orbital calculation[41] which indicates that the carbonium ion bridge will incline towards one of the double bonds with an appreciable activation energy for bridge flipping between the two equivalent positions. Thus, while all three components participate in electron delocalization, only two do so simultaneously. Later work has supported this view.[42]

A molecular orbital treatment has been made on the energetic consequences of electronic delocalization between either two or three non-planar sites,[43] which agrees with the

high heat of hydrogenation of barrelene and the observed electronic interactions in the norbornenyl and norbornadienyl cations. It also predicted stabilization of the 4-bicyclo (3,2,2) nonatrienyl anion (IX) which has been observed[44]. The proton magnetic resonance spectrum of the stable anion solution indicates interaction of the allyl anion bridge with both vinyl bridges and hence this may constitute the first direct observation of electron delocalization between three non-planar components. If the interaction with both bridges is due to bridge flipping, as is the case with the 7-norbornadienyl cation, the energy barrier to flipping must be considerably smaller (< 11.8 Kcal./mole as compared to > 19.6 Kcal/mole). There is, as yet, no evidence to suggest whether this is likely.

The intention of the preceding part has been to give an outline of the more recent development of studies of aromaticity before indicating the area covered by this work. Before doing this, two further notes must be added.

1. <u>Woodward-Hoffmann Rules</u>

The application by Woodward and Hoffmann of considerations of orbital symmetry to the transition states of concerted reactions, consequently explaining many facts which were previously known but not understood and suggesting many further experiments is an event of major importance. It is comparable with any advance made in understanding the static systems previously described. Fortunately the subject has been well reviewed.[45]

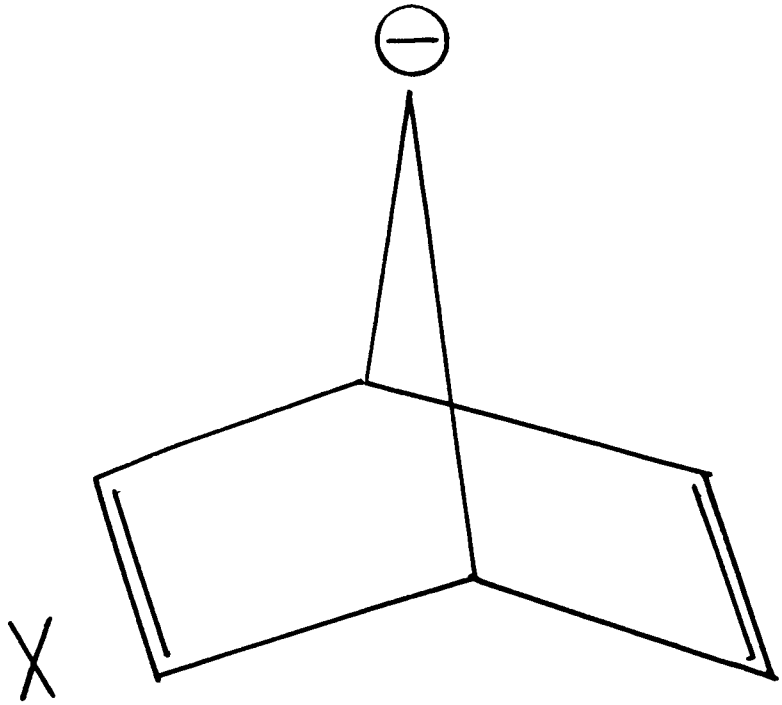
2. Antiaromaticity

The prediction of electronic stabilization of monocyclic coplanar 4n + 2 π-electron systems leaves open the question of whether monocyclic coplanar 4n π-electron systems suffer electronic destabilization. Until recently no unambiguous evidence was available. The instability of cyclobutadiene[46] in which 4 π-electron delocalization is expected and the non-planarity and consequent avoidance of delocalization in cyclooctatatraene are both explicable in steric terms.

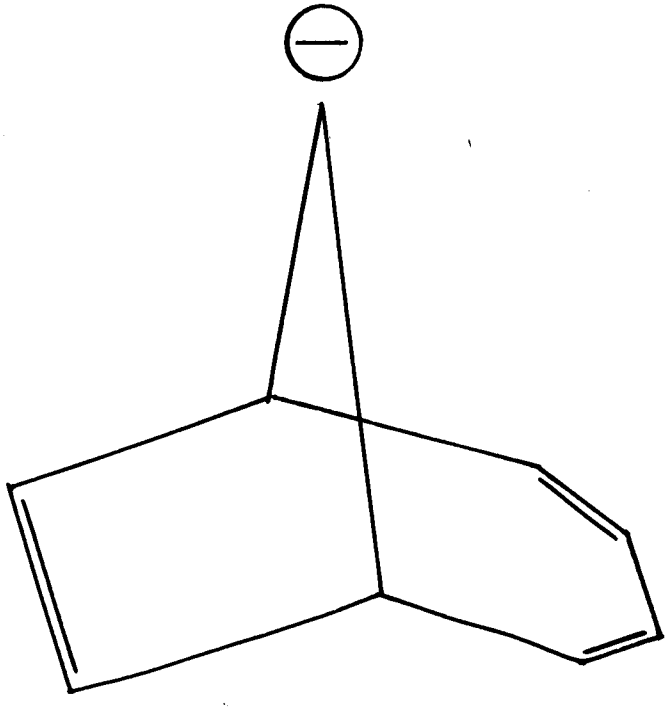
However, practical studies of cyclopropenyl systems have provided qualitative,[47] semi-quantitative[48] and quantitative[49,50] evidence of their reluctance to form the 4 π-electron cyclopropenide anions, supported by molecular orbital calculations indicating thermodynamic destabilization in these systems, i.e. "antiaromaticity" The subsidiary criterion of the nature of proton chemical shifts may also be applied. Pople and Untch have pointed out that in planar monocyclic 4n π-electron rings a paramagnetic ring current would be expected, causing movements of proton chemical shifts in the opposite direction to those of the aromatic 4n + 2 π-electron systems[51] and quoted examples of this phenomenon.

Scope of this Work.

In this work it is intended to examine non-planar anion systems for evidence of electron delocalization of either a stabilizing or destabilizing nature. The specific systems chosen for examination are the 7-bicyclo (2,2,1) heptadienyl



X



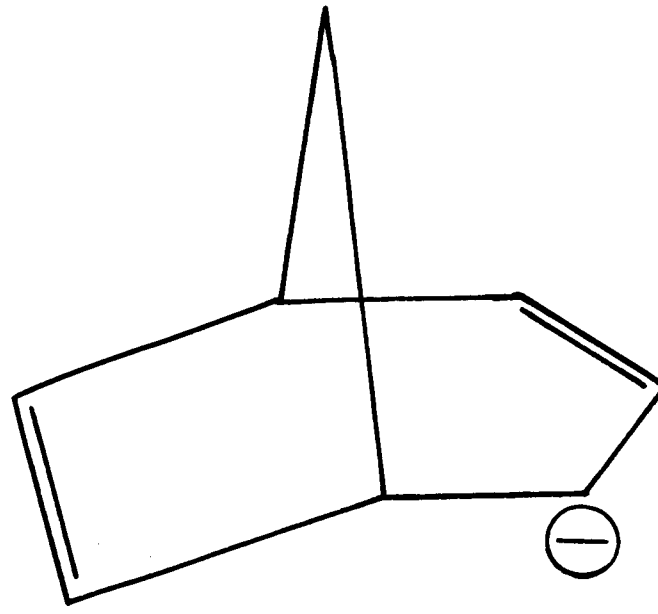
XI

anion (X) and the 9-bicyclo (4,2,1) nonatrienyl anion(XI) (both shown as classical forms) and anion systems derived by reduction of the double bonds present in these systems. Examples of electron delocalization in non-planar anions and in bicyclo (2,2,1) and bicyclo (4,2,1) systems of any charge type which are also of interest will now be described.

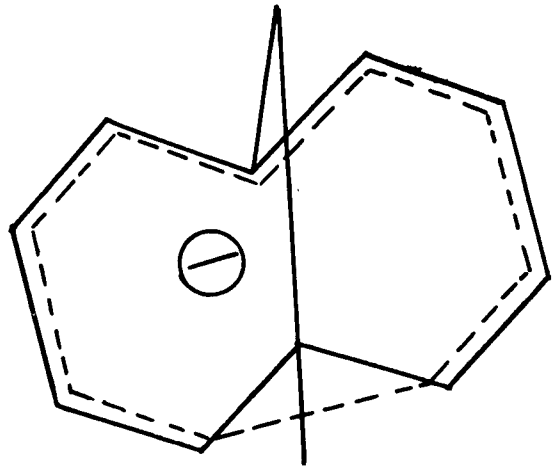
ELECTRON DELOCALIZATION IN SYSTEMS RELEVANT TO THIS WORK

The first observationof electronic delocalization between non-coplanar components in an anion system was made by Brown and Occolowitz[52]. They showed that bicyclo (3,2,1) octa-2,6-diene underwent base-catalysed hydrogen-isotope exchange with dimethyl sulphoxide containing potassium t-butoxide exclusively at the 4-position 10^4 times faster than bicyclo (3,2,1) oct-2-ene or cyclohexene.

They suggested that this was due to stabilizing interaction between the allyl anion portion of the 4-bicyclo (3,2,1) octa-2,6-dienyl anion (XII) and the non-conjugated double bond to give the non-planar equivalent of the cyclopentadienyl anion. This hypothesis was confirmed by observation of the proton magnetic resonance spectrum of the potassium salt generated by cleavage of the 4-methyl ether with sodium-potassium alloy.[53] The spectrum shows extensive



XII



XIII

delocalization of negative charge to the C_6 and C_7 positions and an upfield shift of the C_8 protons consistent with a partially developed ring current. These findings were confirmed by Winstein et.al.[54] Winstein has also observed electron delocalization in the 4-bicyclo (3,2,2) nonatrienyl anion as described previously.[44]

Electron delocalization has been observed in a third non-planar anion by the same technique. Addition of the methylsulphinyl carbanion to 1,6-methanocyclodecapentaene gives an anion (XIII) in which the vinyl proton resonances of the two halves of the molecule are equivalent indicating complete delocalization of the negative charge.[55]

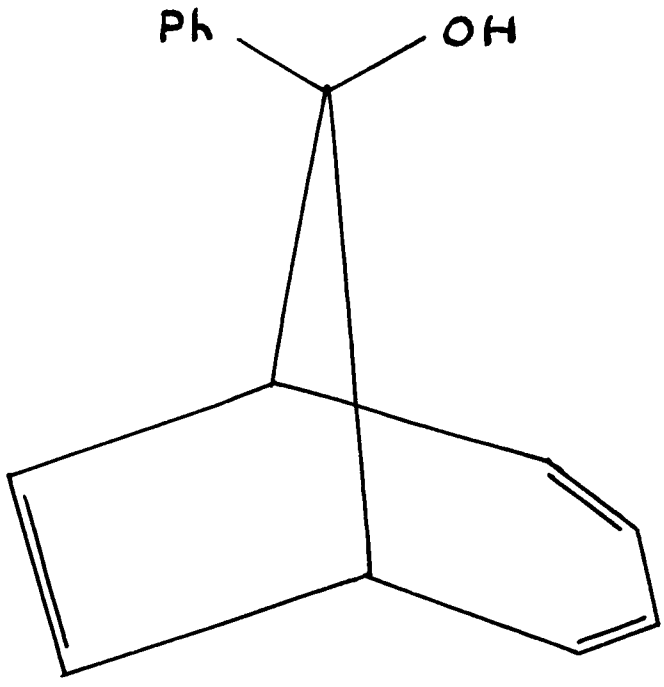
Although small in number these three well founded examples show that electronic delocalization between non-planar components in anion systems is possible and suggest that investigations in other systems, particularly those in which electron delocalization occurs in carbonium ions and radicals, may well prove fruitful.

Of the two systems chosen for study there is much greater evidence of electron delocalization in (2,2,1) than (4,2,1) systems. The kinetic evidence for delocalization in the 7-norbornenyl cation system has already been quoted,[31] as has the kinetic evidence for the norbornadienyl cation[39] which was fully supported by the observation of the proton

magnetic resonance spectrum of the stable cation.[40]

Recently it has been suggested that electron delocalization occurs in the 7-norbornenyl radical.[56] Reduction of either syn- or anti-7-bromonorbornene with tri-n-butyltin deuteride in hexane, which is a known method of generating a free radical, leads to the same 7-deuterionorbornene, probably the anti-compound. This stereochemical result cannot be easily accounted for by a single classical radical or equilibrating classical radicals and thus suggests a three centre delocalized radical. This has been strongly supported by a recent molecular orbital calculation.[57] No evidence has been obtained for a 7-norbornenyl or 7-norbornadienyl anion. It has been suggested that a negative charge at the 7 position may be stabilized by interaction with the dichloroethylene double bond of a substituted norbornene,[58] but this is completely unsubstantiated.

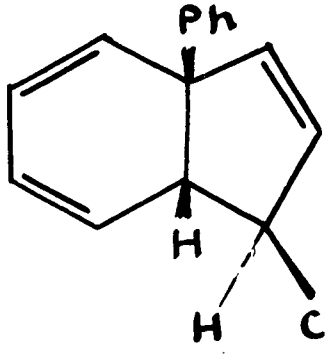
No clear evidence for the interaction of ions or radicals generated on the single carbon bridge of bicyclo (4,2,1) system with π-electrons in other parts of the molecule has yet been obtained. However, only one attempt to do so has been made. Treatment of the bicyclic alcohol (XIV) with thionyl chloride led to a cis fused dihydroindene. (XV) while treatment with p-toluene-



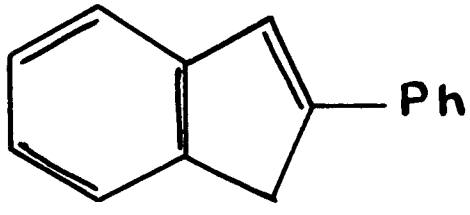
XIV

$SOCl_2$

p—T_sOH
IN $CHCl_3$



XV



XVI

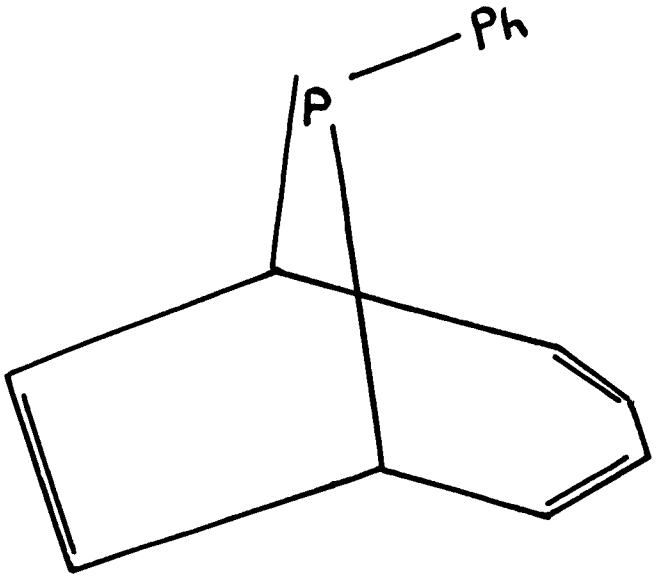
sulphonic acid led to 2-phenylindene.[59] (XVI). No definite details of the mechanisms of these rearrangements are known.

Although no examples of electronic interactions with the single bridgehead position of the (4,2,1) system are known it would seem reasonable that interactions between the single carbon and two carbon bridges might occur since these are in almost the same steric relationship as in norbornene derivatives where interaction has been shown to occur.

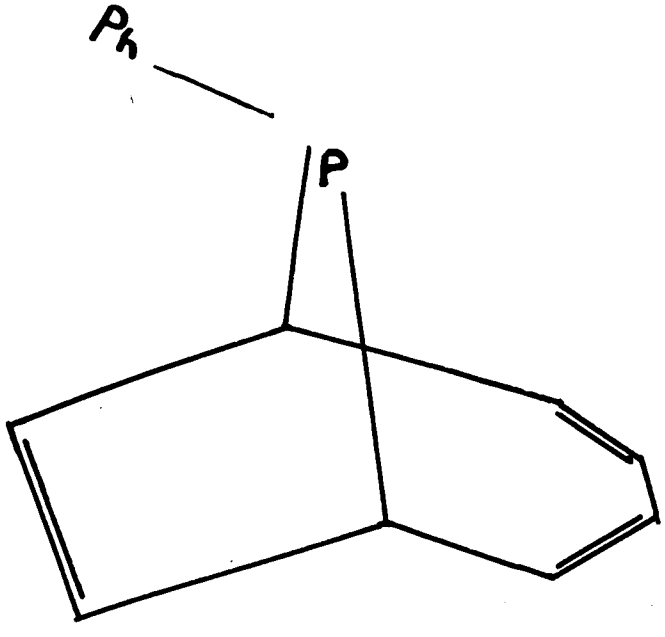
An interesting related compound is 9-phenyl-9-phosphabicyclo (4,2,1) nonatriene, both isomers of which have been prepared[60] (XVII a,b). These compounds are both isoelectronic with the 9-phenyl-9-bicyclo (4,2,1) nonatrienyl anion which it is hoped to generate. The proton magnetic resonance spectrum of neither compound shows any evidence of interaction between the phosphorus lone pair and the ring π-electrons. This is not too discouraging since both the geometry and the electron energy levels will be somewhat different in the phosphorus compound as compared with the carbanion analogue.

KINETIC AND THERMODYNAMIC ACIDITIES

By choice of appropriate starting materials and methods, as described in the next chapter, it was hoped that, in some cases



XVIIa



XVIIb

at least, it would be possible to generate a stable carbanion solution which could be observed by proton magnetic resonance spectroscopy, the simplest available method of obtaining direct evidence of electron delocalization. The conditions employed promoted isotopic exchange with the deuterated solvent and it is from these kinetic results that attempts to determine the thermodynamic properties of the carbanions through which the reactions pass must be made.

Thermodynamics relates the free energy change for a reaction (ΔG) to the equilibrium constant (K) of the mixture of reactants and products thus,

$$\Delta G = - RT \log_e K$$

but there is no apparent connection with the rate of attainment of equilibrium. The most general attempt to provide a correlation is given by transition state theory. This suggests that reaction takes place via an activated complex and that the rate of the reaction is equal to the product of the concentration of activated complexes and the average velocity with which a complex moves to the product side. The assumption that the activated complex is in equilibrium with the products then permits direct relationship between thermodynamic quantities and reaction rates.

The transition state theory is open to objection on several grounds; one of them being that an activated complex, which must lie at a free energy maximum cannot be regarded as a state of equilibrium which corresponds to a free energy minimum. Although the transition state theory has achieved some fair successes, its application has been far from universal and any judgement of whether a correlation between thermodynamic and kinetic acidities of the carbon acids studied here exists requires a more detailed study of the subject.

The very requirement of a relationship between kinetic and thermodynamic acidities only arises because of the difficulties of determining the thermodynamic quantities themselves and so it is not surprising that this relationship should only have been tested in a few cases. The equilibrium constant (K_A) for the ionization of an acid RH thus

$$RH \rightleftharpoons R^- + H^+$$

is defined by the relationship

$$KA = \frac{a_{R^-}\, a_{H^+}}{a_{RH}} = \frac{[R^-][H^+]}{[RH]} \times \frac{f_{R^-} f_{H^+}}{f_{RH}}$$

where a and f indicate the activities and activity coefficients of the appropriate species; and the function pK_A is defined by the relationship.

$$pK_A = - \log_{10} K_A$$

Comparison with the relationship given previously thus shows that pK_A for a substance should be directly proportional to the free energy change involved in ionization and calculable from the relationship.

$$\Delta G = 2.303\ RT\ {}_{p}K_A.$$

The measurements of pK_A S for strong acids (or pK_B S for strong bases) is comparatively simple. The estimation of the concentration of the acid present in the ionized and non-ionized forms is normally possible by a spectrophotometric method using a dilute solution in which it is permissible to equate the concentration and the activity of a species. In the case of weak acids, in order to have a measurable amount present in the ionized form a concentrated solution must be made up, or in more extreme cases a strongly basic species added to assist ionization.

In such solutions, concentrations and activities may be widely different and the estimation of concentrations of the species is made more difficult by the possibility of the aggregation of ions. To deal with this simplifying assumptions have to be made. If two weak acids R_1H and R_2H are present together in the same basic medium, the pK_A S and activities of the various species present are related thus,

$$pK_{A_1} - pK_{A_2} = \log_{10} \frac{a_{R^-_2}}{a_{R_2H}} \frac{a_{R_1H}}{a_{R^-_1}}$$

$$= \log_{10} \frac{R^-_2}{R_2H} \frac{R_1H}{R^-_1}$$

$$+ \log_{10} \frac{f_{R^-_2}}{f_{R_2H}} \frac{f_{R_1H}}{f_{R^-_1}}$$

The first term is normally estimable by a spectrophotometric technique but the second is not. It would be extremely convenient if it were zero or nearly so. The conditions which must be fulfilled for this to be the case is that the ratios of the activity coefficients of uncharged molecule and derived anion should be the same for both the species present. If this were the case, the pK_A S of a series of acids of gradually increasing strength could be established by measuring the differences in pK_a between successive members until one was reached which was strong enough to have its absolute pK_A measured in dilute solution.

Measurements of pK_a S of weak carbon acids have all been based on this assumption and practice, although the means and media used have varied. The first serious attempt was made by McEwen who measured the equilibria between carbon acids and their metal salts.[61] A more recent thermodynamic acidity scale has been developed by Streitweiser, who measured the equilibrium constants between lithium or caesium cyclohexylamide and the carbon acid on the one hand and cyclohexylamine and the lithium or caesium carbon salt on the other, in cyclohexylamine as solvent. [62]

Attempts to extend these scales as far as the saturated hydrocarbons have been made. Applequist and O'Brien measured the equilibrium constants between various alkyl-, alkenyl-, and aryl lithiums and the appropriate iodides in ether and mixtures of ether and pentane;[63]

$$R_1 Li + R_2I \rightleftarrows R_1I + R_2Li$$

Salinger and Dessy measured approximate equilibrium constants for the reactions of various dialkyl-, dialkenyl, and diaryl-magnesium and mercury compounds with one another in tetrahydrofuran;[64]

$$R_1Mg- + R_2Hg- \rightleftarrows R_1Hg- + R_2Mg-$$

The validity of the results of these investigations as true thermodynamic values to be used for comparison with kinetic measurements rests mainly on their encouraging internal consistency[65] rather than on any rigorous examination and justification of the assumptions made in calculating them.

The first linear relationship between the rate of a kinetic process involving transfer of a proton (k_A) and the dissociation constant of the acid concerned (K_A) was proposed by Bronsted in the form,

$$\log k_A = \alpha \log K_A + \log G_A$$

where α and G_A are constants characteristic of the particular series of reactions. The Bronsted equation has been applied more

widely to oxygen than to carbon acids and in these cases it has been found that good linear plots are only obtained when the structures of the acids are very closely related and the acidity range spans only a few pK_A units.[66]

The most extensive survey of carbon acids was made by Pearson and Dillon.[67] They compared the rates and equilibrium constants for transfer of a proton fromcarbon acids to water. Although the overall correlation between ionization rates and pK_A S is only fair, a moderately good correlation is obtained for carbon acids, which have the same acidifying substituents. Comparison of the rates of exchange of weaker carbon acids obtained by Dessy et al. using deuterium oxide and triethylamine in dimethyl formamide and Shatenshtein using deutero-amide in deutero-ammonia has shown that in both cases a good linear correlation with pK_A applies.[68]

Streitweiser and co-workers have applied a different treatment to carbanions which are stabilized by conjugation with an unsaturated system. Applying simple molecular orbital theory it was found that a linear correlation existed between the pK_A S (McEwen's values) of toluene fluorene and indene and the calculated difference in π-electron delocalization energy between carbanion and parent hydrocarbon.[69] A later study showed a linear correlation between exchange rates in cyclohexylamine - lithium cyclohexylamide and the calculated difference in π-electron energy for arylmethanes.

An alternative formulation of the expression for the equilibrium constant of the acid BH, given previously is,

$$a_{H^+} \frac{f_{B^-}}{f_{BH}} = K_A \frac{[BH]}{[B^-]}$$

If the same assumption is made as previously, viz., that the ratios of the activity coefficients of anion and conjugate acid is the same for different species in the same medium a function h- may be defined.

$$h_- = a_{H^+} \frac{f_{B^-}}{f_{BH}} = K_A \frac{[BH]}{[B^-]}$$

which is calculable and affords a measure of the medium's thermodynamic ability to protonate anions in the same sense as a_{H^+} to which the expression approximates in dilute solution. A function H- analogous to pH may then be defined,

$$H_- = -\log_{10} h_-$$

A review of the subject[71] indicates that this assumption is valid and that by use of the H- acidity scale genuine thermodynamic dissociation constants of weak acids in strongly basic media may be determined. Work by Steiner and Gilbert[72] using acid systems previously established[73] has extended a scale of pK_A values, firmly anchored at one end in dilute aqueous solutions, as far as measuring pK_A values of very weakly acidic hydrocarbons such as triphenylmethane (pK_A = 27.2) in pure dimethyl sulphoxide. By use of dimsyl potassium they were able to assign a pK_A of 31.3 to dimethyl sulphoxide itself and to relate the system to the previous work done in strongly basic media.

A final piece of evidence on the subject of kinetic and thermodynamic acidities is that the methoxide catalyzed rate of racemization of optically active 2-methyl-3-phenylpropionitrile shows a good linear correlation with the H-function in varying methanol-dimethyl sulphoxide mixtures.[74] Since the indicators used were substituted anilines and diphenylamines which form anions in strongly basic media and the H-function has been established as a measure of thermodynamic acidity, this suggests both that the transition state inthis base catalysed exchange behaves as an anion and that the kinetic and thermodynamic acidities of the starting material respond in the same manner and with a linear correlation to changes in the solvent system.

Although the evidence available is far from exhaustive, its self-consistency is encouraging. It would seem that rates of base catalyzed exchange of carbon acids in strongly basic media show a good correlation with the thermodynamic stabilities of the carbanions through which they occur, provided that the carbon acids are of a closely related structural type.

CHAPTER TWO

CHOICE OF STARTING MATERIALS AND METHODS

The choice of methods of generating and studying the carbanions which have been selected for this work involves several factors which are interdependent. The choice of the starting material from which the carbanions are to be generated depends on both its ease of synthesis and the effectiveness with which carbanions can be generated from it. Similarly the method of observation must depend on whether the carbanion can be produced as a stable entity or only as a transient species.

The last of these problems is the easiest one to solve. Proton magnetic resonance spectroscopy provides the most convenient method of observation no matter what the behaviour of the carbanion. If the carbanion can be formed as a stable entity it is the simplest means of providing a clear indication of the electronic structure. If the anion is formed only as a transient in an exchange reaction, by arranging that the exchange is conducted in deuterated medium the rate of exchange, at any specific point in the molecule, can be followed by observing the rate of diminution of the resonance corresponding to that specific proton.

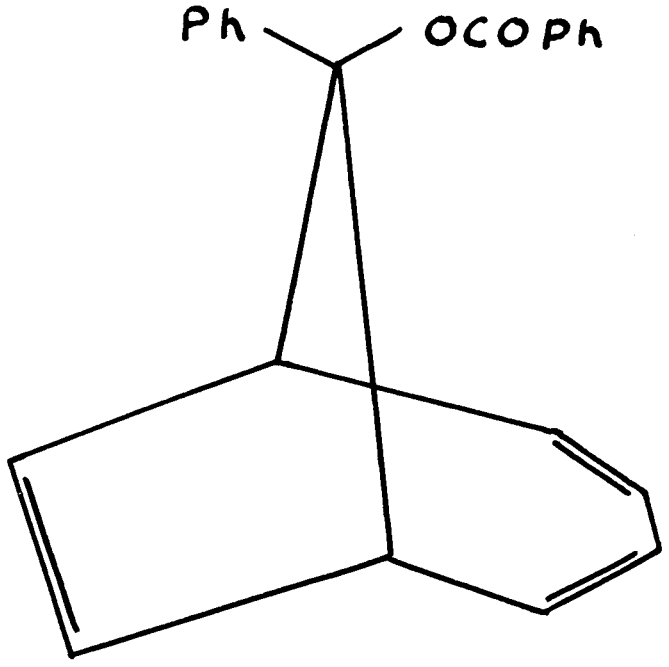
Choice of Starting Materials

The probability that at least some of the carbanions selected for study can only be generated as transients in exchange reactions suggests that the carbanions should be generated by base

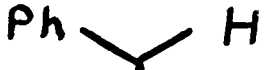
catalysed abstraction of a proton from a hydrocarbon. The characteristics of several of the strongly basic media used in this method have been closely studied, and also the relationship between the thermodynamic stability of the carbanion and this particular rate process has been studied far more intensely than any other, as previously described.

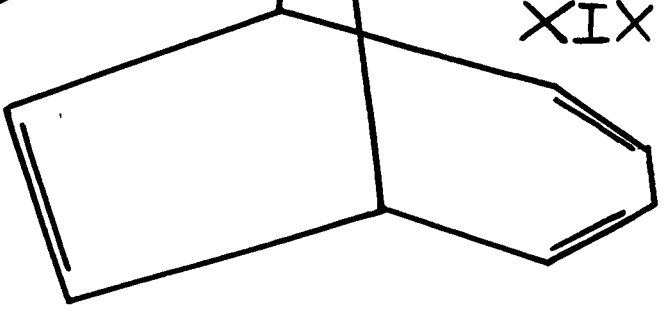
One other apparently promising method was investigated. The single stage synthesis of 9-benzoyloxy-9-phenyl bicyclo (4,2,1) nonatriene (XVIII) in good yield had previously been noted in the literature.[75] It isknown that treatment of carboxylic esters with alkali metals in liquid ammonia may in some cases cause alkyl-oxygen fission.[76] This would have led directly to one of the required anions which might have been sufficiently stable to be observed directly or, by abstracting a proton from a suitable donor, would have given 9-phenyl bicyclo (4,2,1) nonatriene the appropriate starting material for base catalysed exchange reactions in this series.

Unfortunately, using lithium in liquid ammonia, which has been shown to be the system most favouring alkyl-oxygen fission,[77] the predominant reaction was acyl-oxygen fission leading to the bicyclic alcohol which was of no further use. Accordingly this approachwas abandoned and it was decided to concentrate on the use of hydrocarbons and strongly basic media to generate the carbanions.

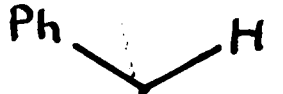


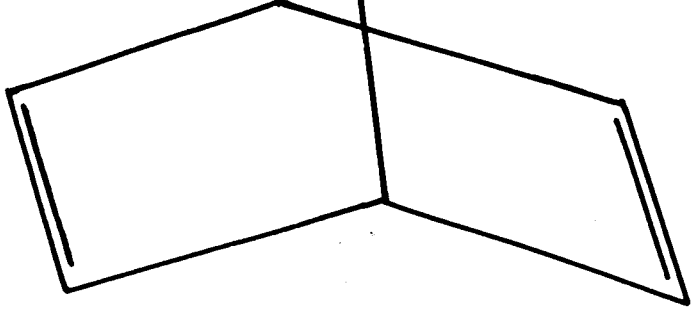
XVIII





XIX





XX

The cleavage of carbon-hydrogen bonds is a process which occurs only with extreme difficulty in the absence of some stabilizing influence on the carbanion formed.[73] In some of the systems studied interaction with the π-electrons of the molecule may provide this influence. This cannot be the case in saturated reference compounds and there is also the possibility that destabilizing electron overlap may occur which would make carbanion formation even more difficult. Consequently it was decided to synthesize starting materials in which the position at which the carbanion would be generated had a carbanion stabilizing substituent attached to it. If the substituent has too great a stabilizing effect on the carbanion it will completely obscure the effects of interaction with π-electrons in other parts of the molecule. For this reason it was decided to use a phenyl group as the carbanion stabilizing substituent rather than the groups with a more powerful effect such as nitro- and cyano-. The primary compounds then required are 9-phenylbicyclo (4,2,1) nonatriene (XIX) and 7-phenylbicyclo (2,2,1) heptadiene (XX). The particular isomer of (XIX) shown is that which was synthesized. These compounds contain the maximum number of double bonds which can be present in their systems. It was hoped to completely hydrogenate the olefinic double bonds in order to provide systems in which the carbanion cannot suffer interaction with double bonds in these arrangements, and also by choice of suitable techniques to selectively

hydrogenate some of the double bonds, so as to determine more precisely the nature of any effects operating.

The evidence which suggests that the phenyl groups will have the desired effect in labilizing the proton it is wished to remove is described in the next section. Other effects which will operate in the benzyl carbanions which it has now been chosen to generate are also described in order to facilitate discussion later.

Effects Operating in Benzyl Carbanions.

The qualitative acidifying effects of phenyl groups on adjacent protons was demonstrated by Shatenshtein[79] and quantitative results were provided by the work of Streitweiser who obtained the following relative rates of detritiation of tritiated hydrocarbons by alkali cyclohexylamides in cyclohexylamine.[80]

Relative Rates of Detritiation

Cyclohexane-t	1 x 10^{-10}
Triptycene-1-t	2.2 x 10^{-3}
Toluene-α-t	1
Diphenylmethane-α-t	270
Triphenylmethane-α-t	1100

The increase in relative rate in passing from toluene to triphenylmethane is in marked contrast to the fall

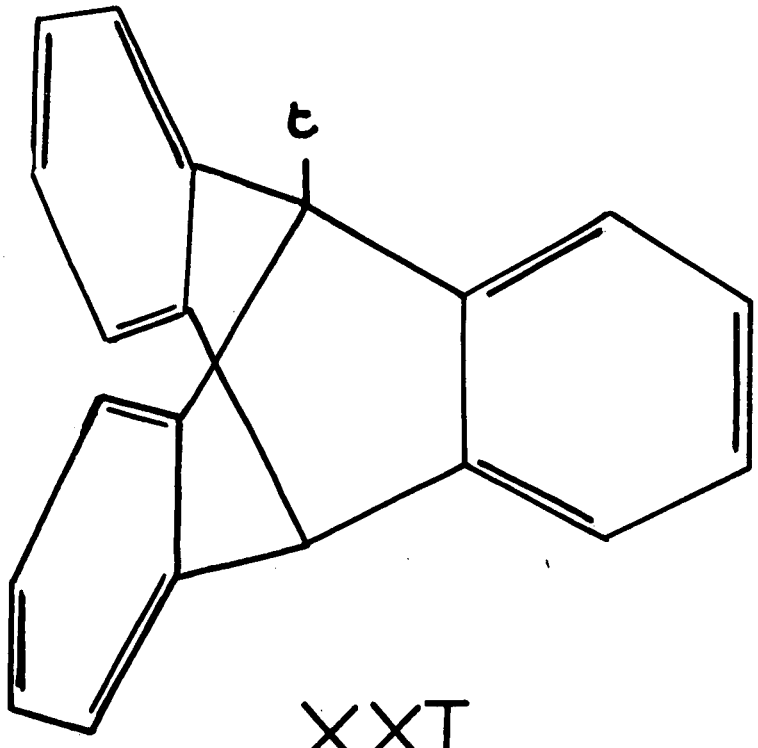
in kinetic acidity which occurs when the α-hydrogens of toluene are replaced by alkyl groups,[81] reflecting the normal decrease in stability on passing from a primary to a tertiary carbanion.

Relative Rates of Proton Exchange

Toluene-α-h	1
Ethylbenzene-α-h	0.22
Cumene-α-h	0.023

Streitweiser suggests that approximately half the labilizing effect demonstrated in triphenyl methane is due to conjugation of a planar Sp^2 - p carbanion with the phenyl rings (although conjugation with all three rings is not possible at the same time) and half is due to a simple inductive effect, as shown by the increased rate of detritiation of triptycene-1-t (XXI) when the carbanion generated is rigidly held non-planar.

The tendency of the benzyl carbanions to assume a planar, fully conjugated, structure with the negative charge occupying a pure p-orbital is opposed by an alternative energetic consideration. A near linear correlation between the estimated pK_A S of a series of hydrocarbons and the percentage S-character of the carbon-hydrogen bond broken has been noted[82] and this has been reinforced by a study which owes nothing to estimation.



XXI

Streitweiser et al [83] have obtained a good correlation between the base catalyzed rates of tritium incorporation of cycloalkanes and their ^{13}C-H coupling constants which give a quantitative measure of the S-character of the carbon-hydrogen bond.[84] By this means they have shown that the carbanion intermediates in the base catalyzed tritiation of medium-size cycloalkanes are pyramidal.[85] The increasing stability of carbanions as their S-character increases is probably due to the lesser shielding of S-electrons from the nuclear charge, as compared to p-electrons, with consequent increase in the Coulomb interaction energy.

Because of these two conflicting effects the most stable configuration of benzyl carbanions isprobably somewhere between planar and pyramidal. Evidence in support of this belief is provided by a study of the charge distributions of various aryl substituted carbanions.[86] In benzyl lithium 38% of the charge is located at the α-position and the rest is delocalized around the aromatic nucleus in accord with a flattened pyramidal structure.

It seems likely that the phenyl group will make possible the removal of the benzylic bridge proton under conditions which will not cause the removal of any other protons in the molecules studied. If this is so it will simpify the analysis of kinetic results. The use of phenyl substituted starting materials has two further beneficial effects. By reducing the number of bridge

protons from two to one it again simplifies the analysis of kinetic results and the presence of the phenyl group increases the solubility of the starting materials in the strongly basic medium chosen for the generation of carbanions.

Choice of Medium for Generating Carbanions.

The particular medium chosen for the generation of carbanions should ideally fulfill certain conditions. It should be as strongly basic as possible in order to optimize the chances of the carbanion being generated as a stable entity which may be directly observed. If this proves to be impossible and the carbanion properties are inferred from the rate of exchange of a proton with a deuterated medium the carbanion like transition-state should be close in energy and geometry to a free carbanion intermediate. In particular the rate and course of the reaction should depend principally on the properties of the transition state itself and not upon the microscopic environment in which the reaction takes place. If the latter is the case, the rate of exchange, and especially the stereochemical course of exchange, give little information about the carbanion itself. The results of such processes can also be extremely complex and difficult to interpret.[87]

The best indication of whether the results of a reaction reflect the properties of a carbanion, rather than those

of a reaction medium, is given by the stereochemical course when an optically active substance is involved. If conjugative stabilization leads to a planar carbanion reprotonation will inevitably give a completely racemic product. If in absence of such stabilization the carbanionformed is pyramidal it should undergo rapid inversion, by analogy with the amines with which it is isoelectronic, and also give a completely racemic product. That this rapid inversion occurs is indicated by the long gap from 1936, when the first study using optically active materials was made,[88] to 1955 when Cram et al. observed the carbonation of an optically active alkyl lithium with a slight overall retention of configuration;[89] the first observation of stereo selectivity in a carbanion reaction. It would seem reasonable that if the extreme cases of both planar and pyramidal forms of carbanion lead to a racemic product any intermediate structure should also lead to a racemic product.

If the evidence of carbanion properties is kinetic the medium chosen should promote an exchange reaction which is of simple kinetic form and is relatively insensitive to any minor inadvertent changes which may occur in the composition of the medium. It will be a further advantage if the medium is stable over a large temperature range thus allowing the choice of conditions where the rate of exchange is convenient for measurement.

Fortunately a system has been discovered which fulfills these requirements. The high activity of a solution of potassium t-butoxide in dimethyl sulphoxide in carbanion generating reactions was first noticed by Cram et al.[80] and studies by Schriesheim et al. have indicated its particular suitability in other respects.[81]

Experiments showed that weakly acidic hydrocarbons exchange protons with dimethyl sulphoxide under the influence of potassium t-butoxide. Hence by placing a hydrocarbon in perdeuterated dimethyl sulphoxide solution with potassium t-butoxide the exchange rate at any molecular position may be measured by observing the rate of disappearance of the proton magnetic resonance signal corresponding to the proton at that point. The exchange rate over all positions of the molecule corresponds to the rate of appearance of protons in the dimethyl sulphoxide. Alternatively, the rate of increase of radioactivity of the olefin when tritiated dimethyl sulphoxide is used may be followed.

Using the latter method, experiments on toluene showed[81] that, at any given temperature and toluene concentration, the rate of exchange is approximately proportional to the concentration of base until the t-butoxide concentration reaches 0.3M, and is almost constant when the t-butoxide concentration is above 0.4M. Presumably this occurs because additional t-butoxide increases the size of ion

aggregates which are formed without increasing the activity of the base. At these higher t-butoxide concentrations the exchange reaction is first order depending only on toluene concentration at the temperatures investigated from 23.5° to 60° and the energy of activation is 18.2 ± 0.4 kcal. The first order rate constant is almost unaltered by changes in toluene concentration from 0.1 to 0.4M. The rates of exchange at the α-positions of a series of phenyl substituted hydrocarbons are in very good qualitative agreement with the results of the same base catalyzed exchanges using ammonia-potassium amide[79] and cyclohexylamine-potassium cyclohexylamide.[91]

An advantage of t-butoxide in dimethyl sulphoxide is that it only causes the exchange of benzylic protons in the compounds studied whereas the other base systems also cause the exchange of aromatic ring protons. If this also applies to the compounds studied in this work it will simplify the interpretation of the kinetic results. The insensitivity of the rate constant to variation in the concentration of t-butoxide and olefin should minimize differences due to small inadvertent differences in composition of samples used to measure the same rate constant.

Later work has shown that toluene in dimethyl sulphoxide-potassium t-butoxide shows a hydrogen-deuterium isotope effect (K_H/K_D) of about 0.6[92] This suggests a reaction scheme as below,

$$C - H + B^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \cdots HB \xrightarrow{DB} C \cdots DB \xrightarrow{k_{-1}} C - D + B^- \xrightarrow{k_2}$$

in which $K_{-1} >> K_2$, i.e. the rate of dissociation is faster than the rate of exchange and the rate determining step does not involve the breaking of a covalent carbon-hydrogen bond which would show a positive hydrogen-deuterium isotope effect. On this basis the rate determining step is the reorganization of the solvent around a carbanion. This is encouraging since it suggests that the reaction proceeds through a free carbanion intermediate and will reflect the properties of the carbanion rather than the solvent medium.

As would be expected from this argument the vast majority of exchanges carried out under these conditions on optically active substances lead to total racemization. In cases where exchange does occur with some stereospecificity, as e.g. carbanions with attached sulphone groups, the stereospecificity is lower in this medium than in any other and may be explained by effects operating in the carbanions themselves, since a planar carbanion of this type would suffer from destabilizing Coulombic interactions between the negative charge located on carbon and the partially charged oxygen atoms of the sulphone group.

For the reasons given previously it would seem that potassium t-butoxide in dimethyl sulphoxide provides a suitable and well characterized medium for the study of the carbanions which it is hoped to generate, and so it has been selected for this work.

CHAPTER THREE

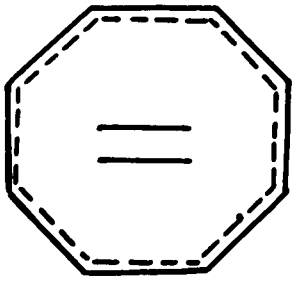
SYNTHESIS OF STARTING MATERIALS

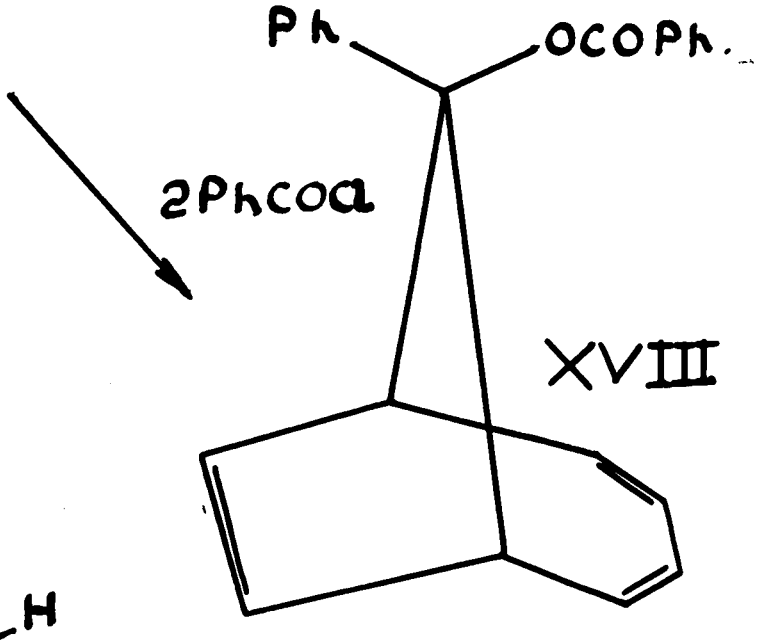
Attempted Synthesis of 9-phenylbicyclo (4,2,1) nonatriene

A. Via Ester Cleavage

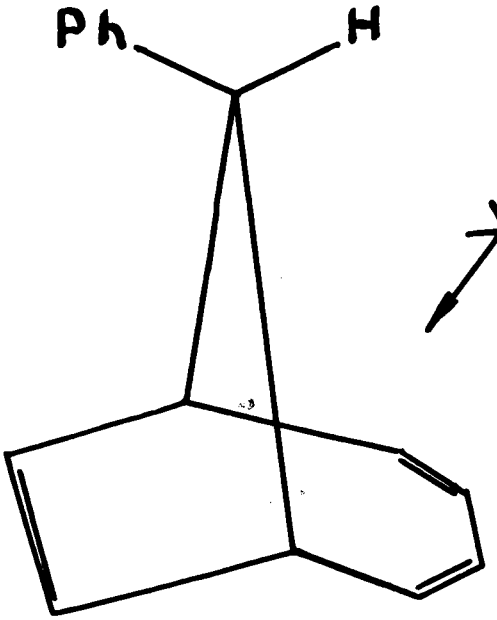
The first attempt to synthesize 9-phenylbicyclo (4,2,1) nonatriene (XIX) was made via 9-benzoyloxy-9-phenylbicyclo(4,2,1) nonatriene (XVIII); prompted by a report[75] of the synthesis of this compound in good yield by a single step process. At the time this preparation was attempted it was known that a mixture of products was produded but no practical details were available. A personal enquiry to the authors obtained practical details after several months had elapsed. By that time experiments on the somewhat impure material obtained had made it seem likely that this method would not give the desired starting material. A full report of the reaction of cyclooctatetraene dianion with benzoyl chloride and of other acylation reactions of cyclooctatetraene has since been published.[10]

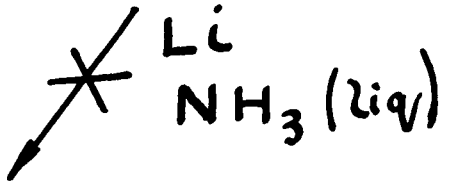
It seems that the somewhat forbidding product, obtained under the conditions initially used was essentially the same as that obtained by Cantrell and Shechter, and so it is not surprising that a series of modifications did not significantly improve its form. The work up of the product followed much the same course as that of Cantrell and Shechter except that they extracted a minor product before attempting to crystallize the major one.





XVIII





XIX

The material which was finally obtained, although impure, was essentially 9-benzoyloxy-9-phenylbicyclo (4,2,1) nonatriene (XVIII) as indicated by the physical data. The clearest indication was given by N.M.R. The areas of the peaks not corresponding to those of the major product showed that the material obtained was certainly over 90% pure and probably over 95% pure.

In the hope that monoacylation, to give the bicyclic alcohol, might yield a more tractable product, and particularly one with functionality which would aid separation of the reaction mixture, cyclooctatetraene dianion was treated with one equivalent of benzoyl chloride. The product of this reaction did appear to be mainly the bicyclic alcohol but the product was no more susceptible to the normal techniques of purification than the crude ester products obtained previously. An attempt to separate the bicyclic alcohol by the monoesterification of phthalic anhydride to produce an acid phthalate, which could be extracted by alkali, failed.

It is known that the cleavage of esters by alkali metals dissolved in liquid ammonia may in some cases proceed by alkyl-oxygen fission, giving a hydrocarbon on protonation,[76] rather than by acyl-oxygen fission to give an alcohol. Detailed studies of the cleavage reaction have shown that its course is influenced by the alkali-metal used.[77] The use of lithium as reducing agent leads to a higher

proportion of alkyl-oxygen fission than that of sodium or potassium and accordingly this was used. The necessity of using the somewhat impure ester, which was the best starting material which could be obtained, made the observation of the course of the reaction slightly more difficult but it seemed clear that cleavage was proceeding almost entirely by acyl-oxygen fission to give the bicyclic alcohol. Approaches to the bicyclic anion through this series of compounds were abandoned and future attempts were all to synthesize the bicyclic hydrocarbon and generate the carbanion by removing a proton with strong base.

B. Via Organometallic Compounds

A promising route to 9-phenylbicyclo (4,2,1) nonatriene was suggested by the thermal rearrangement of bicyclo (6,1,0) nonatriene to bicyclo (4,2,1) nonatriene when attached to a molybdenum complex.[98] The free bicyclo (6,1,0) nonatriene undergoes thermal rearrangement even more readily to give a mixture of cis- and trans - 8,9-dihydroindene.[106] The change in the course of the thermal rearrangement presumably occurs because the molybdenum complex requires that starting material, product, and transition state should all be capable of providing the six π-electrons which give the central molybdenum atom the electronic configuration of the next noble gas, xenon.

The thermal rearrangements of several bicyclo(6,1,0) nonatriene have been investigated. With only one exception[119] the predominant product is always the cis- fused dihydroindene. A thorough

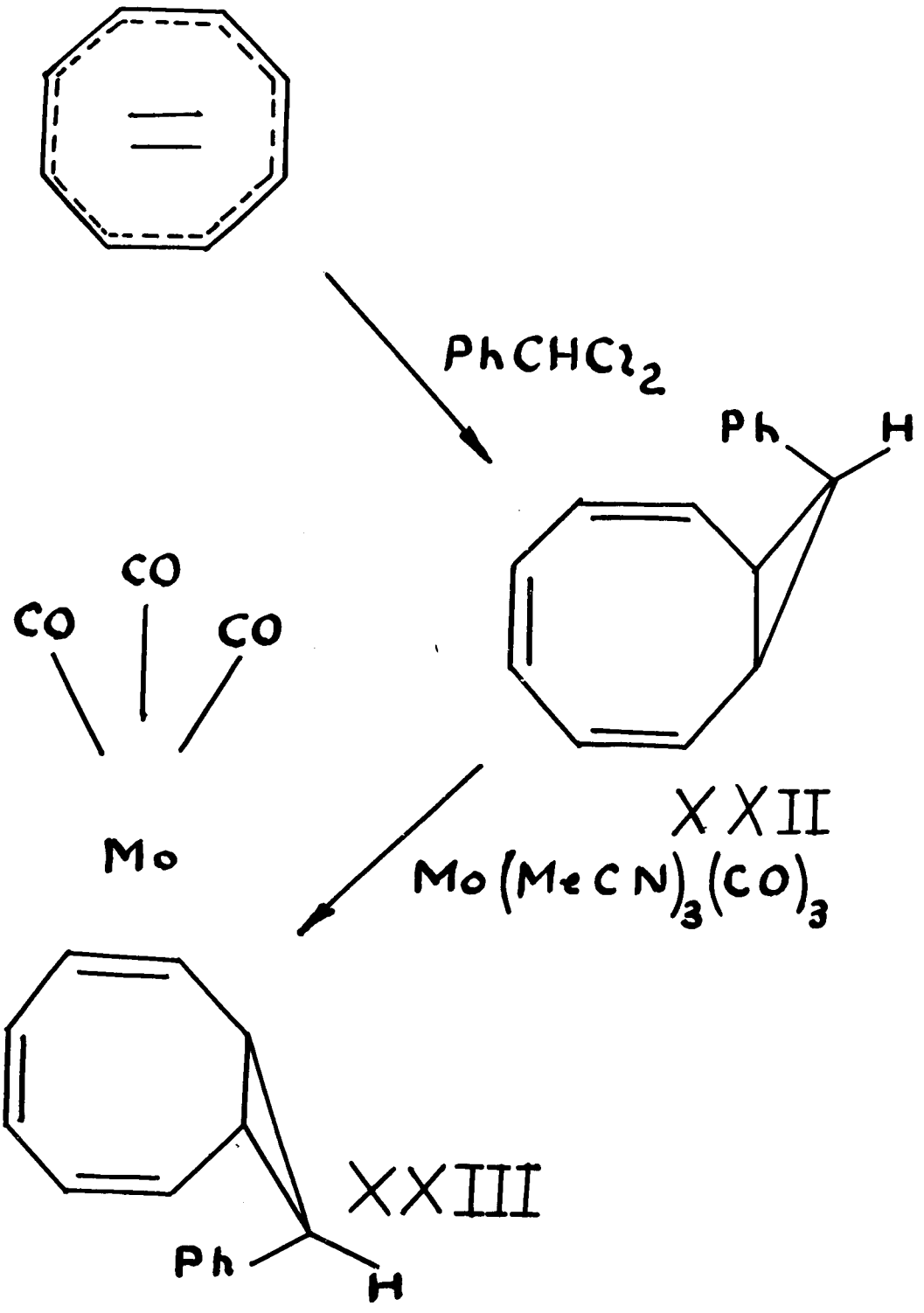
investigation[120] of the thermal rearrangements of syn- and anti-9-methylbicyclo(6,1,0)nonatriene has shown that the reaction proceeds mainly through an all -cis cyclononatetraene, whereas a concerted electrocyclic ring opening of the bicyclononatriene would be predicted to give a cis,cis,cis,trans- cyclononatetraene. The expected disrotatory ring closure of the all-cis cyclononatetraene, once formed, would give the observed cis-fused dihydroindene. The exception observed to this path was that of the rearrangement of 9,9-dimethyl bicyclo (6,1,0) nonatriene which gives mainly the trans - fused dihydroindene.[119] It was suggested that in this case the steric strain caused by the dimethyl substitution at the 9-position prevented the compound assuming the configuration through which the other thermal rearrangements proceeded.

The starting material required for synthesis of 9-phenylbicyclo (4,2,1) nonatriene was 9-phenylbicyclo (6,1,0) nonatriene, the synthesis of which had not previously been reported. However, the formation of compounds of this type by the reaction was cyclooctatetraene dianion with gem-dihalides had been reported[93] and there seemed no reason why this method should not be employed, using benzal chloride as the gem-dihalide. It seemed likely that cyclooctatetraene dianion could be generated more easily in liquid ammonia than in tetrahydrofuran as previously This method gave a good yield of the desired product. Its successful use has since been reported elsewhere.[119] The product was assigned the syn- stereochemistry on the basis of its N.M.R. spectrum. ~~The coupling constant between the basis of its N.M.R. spectrum.~~ The coupling constant between the two bridgehead protons of the cyclopropyl ring and the single proton at the 9- position was 6.5 c/s. Both syn- and anti-isomers of compounds of this type have been prepared. The

coupling constant of the cyclopropyl protons was reported as 7 c/s for *syn*-compounds and 4 c/s for *anti*-compounds.[110]

The route indicated for attachment of the olefin to the molybdenum complex[98] involved conversion of the commercially available molybdenum hexacarbonyl to the tricarbonyl diglyme complex. This was isolated and in turn converted to the tricarbonyl tris (tetrahydrofuran) complex which was treated *in situ* with the olefin. Attempts to follow this route met with complete failure. Although Grimme cited the somewhat fragmentary data available for the preparation of the diglyme complex[99] without further comment this method proved unsuccessful in spite of fairly strenuous efforts involving a series of modifications. All attempts to prepare the diglyme complex either showed no reaction or led to decomposition with precipitation of metallic molybdenum. This suggests that in successful preparations some trace of a catalytic material may have been present. Attempts by other workers to prepare the diglyme complex have also met with failure.[121]

An alternative trisubstituted molybdenum carbonyl which might ultimately lead to the molybdenum tricarbonyl olefin complex was suggested by the report of the very ready preparation[96] of tricarbonyltris (acetonitrile) molybdenum(0). This proved as easy to prepare as reported. The only difficulty in its use was the reported air sensitivity which made it necessary to use it in the next step *in situ*, inevitably leading to the inclusion of


PhCHCl2
Ph
H
CO
CO
CO
Mo
XXII
Mo(MeCN)3(CO)3
XXIII
Ph
H

impurity.

In a series of test experiments it was attempted to use the tris (acetonitrile) complex in place of the diglyme complex for the preparation of the tris (tetrahydrofuran) complex, thus returning to the path originally described.[98] A wide variety of conditions was employed. In all cases but one the ultimate result was decomposition of the complex and oxidation to molybdenum blue, presumably by traces of air which gradually leaked in. In the only case in which this did not occur the much lower frequencies of the carbonyl stretching bands in the product (ν= 1780, 1721) as compared to the carbonyl bands in the mononuclear molybdenum complexes prepared made it almost certain that the product had bridging carbonyl groups.

Because of the failures of these small scale experiments no large scale attempt was made to prepare the tris (tetrahydrofuran) complex. At about that time a report appeared of the preparation of molybdenum olefin complexes by reaction of the tris (acetonitrile) complex directly with olefins.[122] An analogous reaction proved fairly simple. Refluxing the acetonitrile complex with the olefin in cyclohexane, under nitrogen, for six hours gave the desired olefin complex (XXIII) as the major product. The accumulated impurities of two steps made it necessary to extract and recrystallize under nitrogen to obtain a pure product. The structure of the product was confirmed by the physical data.

The carbonyl stretching frequencies (ν = 2003, 1939, 1919) are of similar values to those of the bicyclo (6,1,0) nonatriene complex (ν= 1990, 1925, 1902) prepared previously,[98] suggesting a similar structure and more particularly a mononuclear complex. A mass spectrum of the product was very difficult to obtain and not particularly informative except to establish the molecular weight as that of the mononuclear complex. The olefin was unchanged in structure at this stage and had not undergone thermal rearrangement to a dihydroindene prior to complex formation or to a bicyclo (4,2,1) compound after it. Decomposition of the complex and extraction of the olefinic product showed that this had the same.u.v. spectrum as the starting material. This was confirmed by subsequent experiments. Although lack of time did not permit a thorough investigation of the thermal rearrangement of the uncomplexed olefin, a preliminary experiment, following the course of the reaction by u.v., showed that the olefin required four hours at 140° to undergo complete thermal rearrangement. It is not surprising that refluxing for several hours in cyclohexane (B.pt.81°) produced no appreciable isomerization of the olefin. Rearrangement of the olefin when attached to the complex required even more rigorous conditions, as will be seen.

The co-ordination of the olefin to the metal is through the 6π-electron system of the eight membered ring as hoped rather than through the benzene ring. This is made clear by the extensive

shifts which occur in the positions of the olefinic protons in the N.M.R. spectrum while the phenyl protons are almost completely unaffected, as compared to the uncomplexed olefin.

Once the complex had been successfully prepared the next requirement was for a suitable solvent in which to conduct the rearrangement. Grimme[98] had used n-hexane in sealed tubes heated to 125°. Because of the possibility that overlong heating would cause decomposition of the complex, a system from which samples could be withdrawn at intervals to monitor the course of the reaction was preferred. This required a solvent which boiled no lower than the temperature at which the reaction was being conducted. Also the solvent had to be of very low nucleophilicity to avoid the possibility of displacing the olefin from the complex. The solvent chosen was high boiling petroleum ether, in which aromatic compounds had been reduced to a very low level by repeated nitration. The petroleum ether was split into fractions of 5° boiling range and attempted thermal rearrangements conducted by heating solutions of the complex, under nitrogen, on an oil bath maintained at approximately the middle of the appropriate boiling range. Samples were withdrawn at 30 minute intervals for a period of three hours and examined by I.R. spectroscopy for signs of thermal rearrangement. Prior to the experiment using boiling range 155° - 160° which is described, identical experiments with boiling ranges 120°-125°, 130°-135°, 140°-145°,

had been conducted showing no isomerization whatsoever in three hours; an experiment using boiling range 150° - 155° petroleum ether showed approximately as much change in three hours as the later experiment did in one hour. The attempted rearrangement in 155° - 160° petroleum ether gave none of the rearranged complex desired. The only isolable products were metallic molybdenum and molybdenum hexacarbonyl. Examination of the residue left after removal of the solvent showed that the organic constituents were many and varied and gave no hope of the ready isolation of 9-phenylbicyclo (4,2,1) nonatriene.

The I.R. spectra obtained indicate that the most probable course of the reaction is that the initial complex undergoes thermal rearrangement to give another complex, or possibly several other complexes, which is less stable thermally than the starting material and decomposes to metallic molybdenum, carbon monoxide and one or several organic moieties which may undergo further thermal reactions. The carbon monoxide liberated may then react with either the initial or the intermediate complex displacing the organic moiety to give molybdenum hexacarbonyl. The recarbonylation of tricarbonyl molybdenum complexes to tetracarbonyl molybdenum complexes by carbon monoxide produced <u>in situ</u> has been observed.[111] Further recarbonylation to give molybdenum hexacarbonyl was not observed.

However, in the compounds studied the ligands displaced by carbon monoxide were tertiary phosphines which could be displaced singly. The tridentate nature of the olefinic ligand used makes it necessary that displacement would involve the filling of three co-ordination sites by carbon monoxide to give molybdenum hexacarbonyl. Experiments involving heating a nujol mull of the complex between sodium chloride plates also showed that conditions necessary for reaction lead to decomposition and the production of metallic molybdenum.

The reason why the olefin fails to undergo a similar rearrangement to that of bicyclo (6,1,0) nonatriene when complexed is probably steric. A scale model of the molecule shows that the syn- phenyl group approaches the atoms of the eight membered ring fairly closely. Since the mechanism of the rearrangement has not been established it is difficult to comment on what effect this might have. It is clearly possible, however, that the phenyl group may cause unfavourable steric interactions in a transition state which are not present in the corresponding transition state for rearrangement of the non-phenyl substituted olefin. Alternatively the bulky phenyl-group may cause the olefin to adopt a different conformation before reaction starts leading to an entirely different reaction path as has been suggested to explain the anomalous rearrangement of 9,9-dimethylbicyclo (6,1,0) nonatriene.[119] The thermal rearrangement of uncomplexed 9-phenylbicyclo (6,1,0) nonatriene requires a higher temperature (140°) than that of

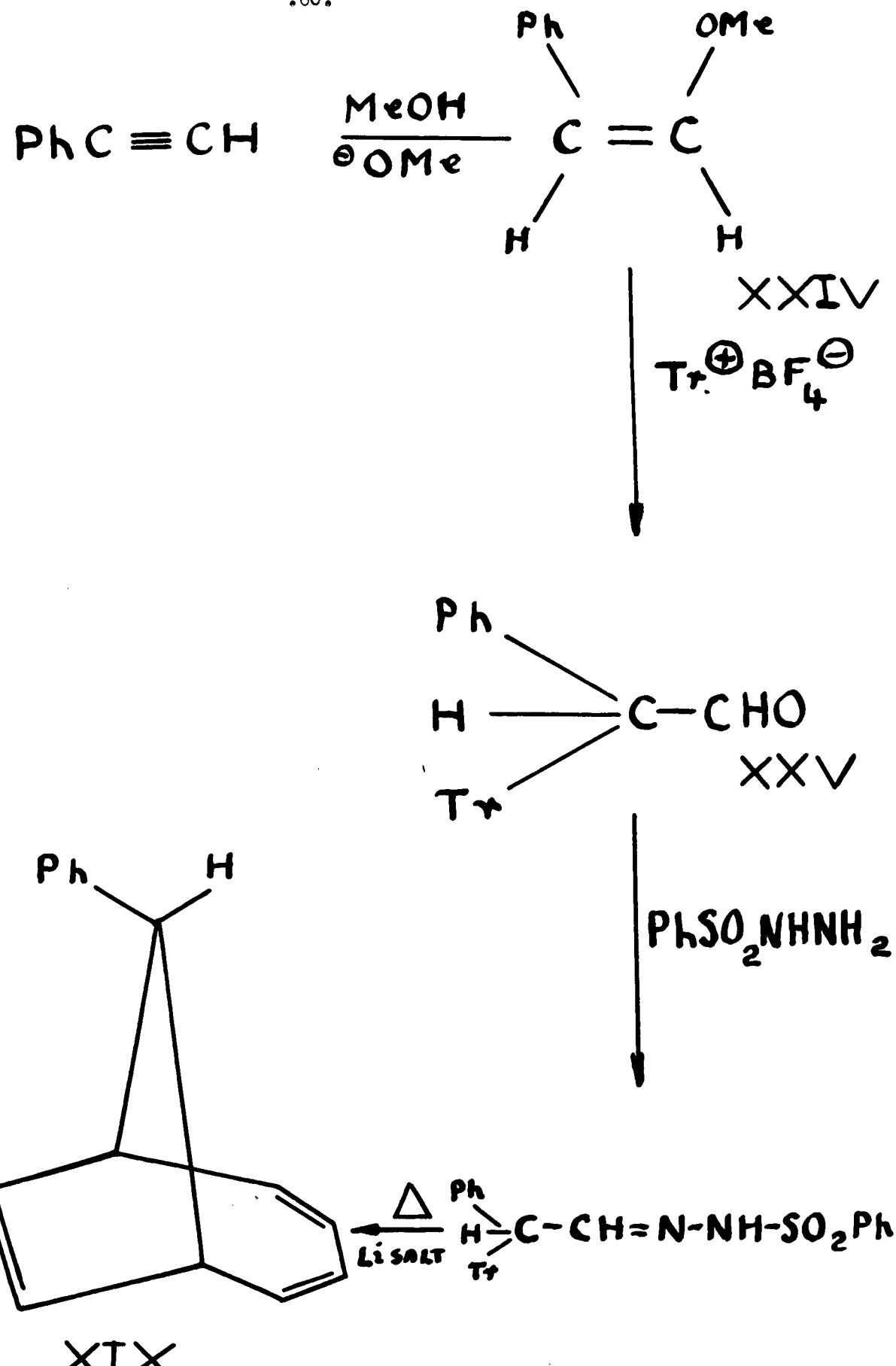
bicyclo (6,1,0) nonatriene[3] (90^{o}) but because the nature of the products was not thoroughly investigated it is impossible to say whether the normal cis- dihydroindene product was being formed or whether this rearrangement is also anomalous giving a trans- dihydroindene as the major product.

The careful monitoring of the course of the attempted thermal rearrangement made it clear that no modification of the reaction conditions was likely to give tricarbonyl (9-phenylbicyclo(4,2,1) nonatriene) molybdenum(0) in good yield. This approach to the synthesis of 9-phenylbicyclo (4,2,1)nonatriene was abandoned.

Synthesis of 9-phenylbicyclo(4,2,1) nonatriene)

During the course of the organometallic work the synthesis of 9-phenylbicyclo (4,2,1) nonatriene (XIX) was first reported,[104] unfortunately in the form of a communication without practical details. The product forming step was the pyrolysis of the tosyl hydrazone of α-phenyl-α (7-tropyl) acetaldehyde to give 9-phenylbicyclo (4,2,1) nonatriene as the major product among several others. This particular step has since been examined in greater detail by the same workers and a further report has appeared.[112]

The synthesis of α-phenyl-α-(7-tropyl) acetaldehyde (XV) was not reported, nor has it been described elsewhere in the literature. The synthesis of α-(7-tropyl) acetaldehyde by means of the addition of tropylium ion to ethyl vinyl ether[105] in aqueous solution had been


PhC≡CH
MeOH
⊖OMe
Ph
OMe
C = C
H
H
XXIV
Tr⊕ BF4⊖
Ph
H — C — CHO
Tr
XXV
PhSO2NHNH2
Ph
H
Δ
Li SALT
Ph
H — C — CH=N-NH-SO2Ph
Tr
XIX

referred to and it seemed probable that addition of tropylium ion to a suitable phenyl-substituted vinyl ether would give the desired product. However, the direct substitution of especially labile α-hydrogen atoms of aldehydes has also been reported.[113] Because of the greater simplicity of this method it was tried first. In a small scale reaction, under the same conditions later used for the reaction of β-methoxystyrene and tropylium fluoroborate, phenylacetaldehyde was treated with tropylium fluoroborate. The reaction product appeared to be mainly polymeric. This was not unexpected since phenylacetaldehyde polymerizes so readily that the starting material bought was not guaranteed free of polymer.

The phenyl-substituted vinyl ether chosen as starting material for the synthesis of α-phenyl-α-(7-tropyl) acetaldehyde was β-methoxystyrene (XXIV). The synthesis of this has been reported, by base catalysed addition of methanol to phenylacetylene[100,101] to give a single product, and by pyrolysis of phenylacetaldehyde dimethyl acetal[100] to give a mixture, presumably of the cis- and trans- isomers possible for β-methoxystyrene. Because of its greater simplicity the base catalyzed addition was chosen. Slight modifications were made to the procedures reported. To enable the course of the reaction to be monitored, by withdrawing aliquots, the reaction was performed by refluxing phenylacetylene with a methanolic solution of sodium methoxide, rather than heating in a sealed tube. Dimethyl sulphoxide was added to the reaction mixture to increase

the activity of methoxide ion and reduce the reaction time necessary at the lower temperature. Product was obtained in moderate yield, identical with that obtained by Miller[100]. His prediction that this would be the *cis-* isomer formed by *trans-* addition of methanol to the acetylenic bond is confirmed by the N.M.R. spectrum of the product. The coupling constant of the vinyl protons (7.2 c/s) corresponds to a *cis-* arrangement about the double bond.[114]

The reaction conditions for the addition of tropylium ion to β-methoxystyrene were found without too much difficulty. An early trial experiment using methanol as solvent showed the importance of choosing a medium in which both reactants were as soluble as possible. In this solvent tropylium fluoroborate was only sparingly soluble and the predominant product of the reaction was phenylacetaldehyde dimethyl acetal formed by acid catalyzed addition of methanol to the double bond. The reaction mixture which proved successful was made up by dissolving the β-methoxystyrene in methanol and adding water to increase the solubility of tropylium fluoroborate until the first traces of cloudiness appeared in the solution. This reaction solution led to a mixture of the free aldehyde and its unhydrolysed dimethylacetal. The free aldehyde was crystallized out and the acetal hydrolyzed under as mild conditions as possible to minimise the possibility of acid catalyzed self-condensation of the aldehyde as it was formed.

In the next stage of the synthesis the benzene sulphonyl hydrazone rather than the toluene sulphonyl hydrazone was used. In the original communication it was stated that the tosyl hydrazone was pyrolyzed in dioxan at 90-95°. In a preliminary experiment the benzene sulphonyl hydrazone was heated in dioxan at 90-95° for 24 hours and aliquots withdrawn at intervals and examined by T.L.C. Although the benzene sulphonyl hydrazone decomposed it gave a complex mixture of products, but no hydrocarbons, which were then the only products reported for the reaction.

A closer survey of the literature indicated that a more normal procedure for the pyrolysis of sulphonyl hydrazones consisted of heating a dry alkali metal salt under high vacuum and collecting the products, which distilled.[115] Accordingly the dry lithium salt of the benzene sulphonyl hydrazone was made and pyrolyzed under high vacuum at 100-105°. The product mixture obtained was complex and although it contained 9-phenylbicyclo (4,2,1) nonatriene, as major product, the separation of this compound in pure form proved difficult and required somewhat complex procedures.

After the pyrolysis had been performed a report appeared of the more detailed study of this step.[112] The method used was to heat the sodium salt of the tosyl hydrazone in dioxan at 80-85°. Besides the two olefins reported previously, 2-phenylindene and two nitrogen containing products, a pyrazole and a pyrazoline were isolated. Under the more vigorous conditions of the dry salt

pyrolysis these nitrogen containing compounds were decomposed before reaching the cold trap. The only evidence obtained formthem was a weak absorption band in the I.R. spectrum in the region expected for a pyrazoline in one of the pyrolyses performed.

The bulk of the product (3.5g.) made it necessary that the means of separation of the olefinic constituents of the product should be column chromatography. Other techniques were used as necessary. N.M.R. was used to confirm the presence of 9-phenyl(bicyclo (4,2,1) nonatriene as the major product and as the prime means of establishing the identity of the final fractions. T.L.C. was used in a series of initial experiments to determine the chromatographic conditions which would give the best separation of the olefins, and also to determine the number of components in any fraction. V.P.C. was used to determine the relative amounts of the components in any fraction, although somewhat cautiously because of the possibility of thermal re-arrangements of some of the products at the elevated temperatures employed. The eluent fractions from column chromatography were submitted to u.v. spectroscopy to determine which fractions contained olefinic product and as a very rough guide to the composition of each fraction. Using these methods it was found that the best procedure was to run the product through a small column initially to remove products other than olefins; these were principally fine particles of starting material which had been carried over. The final separation using a larger column was found to be improved by working at lower temperatures and so this step was carried out ina

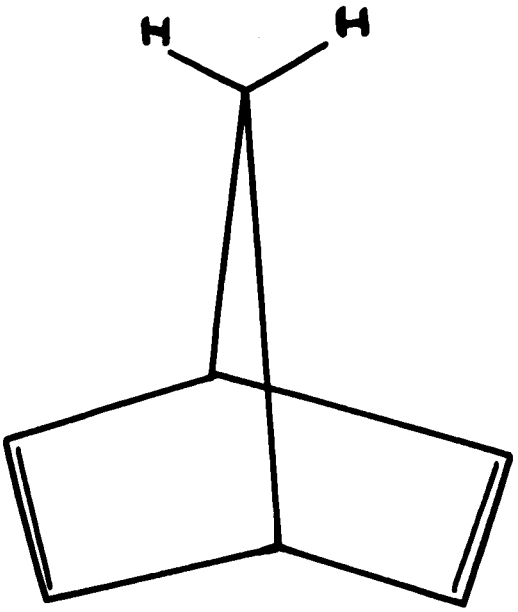
cold room.

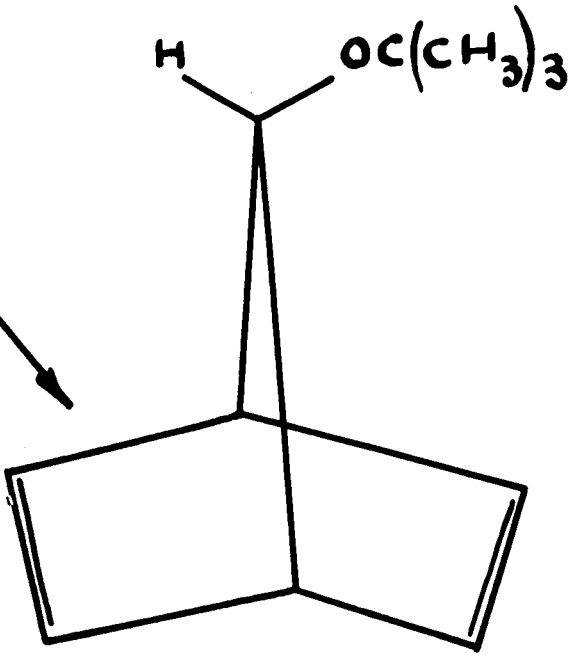
Two sets of fractions seemed to consist mainly of a single compound. The first was adjudged to be 1-phenyl-1-(7-tropyl) ethylene on the basis of its N.M.R. This is simply the product of intramolecular hydrogen transfer in the initially formed carbene and so might be expected. The second compound was 9-phenylbicyclo (4,2,1) nonatriene. One of the fractions crystallized to give material of almost the same melting point as that reported.[112] V.P.C. showed that other fractions in this set consisted almost entirely of the desired product. The increased purity of these fractions made it possible to see that no thermal rearrangement occurred when they were subjected to V.P.C. and also made possible the separation of 9-phenylbicyclo (4,2,1) nonatriene from minor impurities by this method. The material used for kinetic experiments was collected from a V.P.C. column.

Bicycle (4,2,1) nonatriene was prepared by standard methods for the purposes of kinetic comparison.

Synthesis of Bicycle (2.2.1)-compounds.

The synthesis of the key compound in this series, 7-phenylbornadiene has been described.[109] The first stage in the synthesis was the conversion of norbornadiene to 7-t-butoxynorbornadiene(XXVI). The method chosen for this conversion

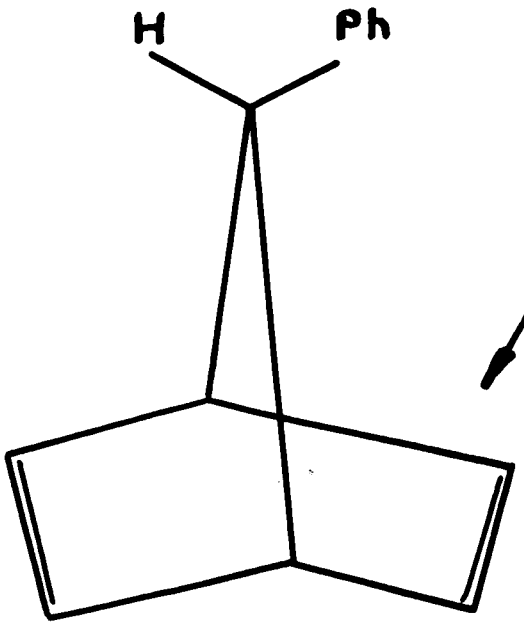




$C_6H_5CO_3C(CH_3)_3$

CuBr

XXVI



PhMgBr

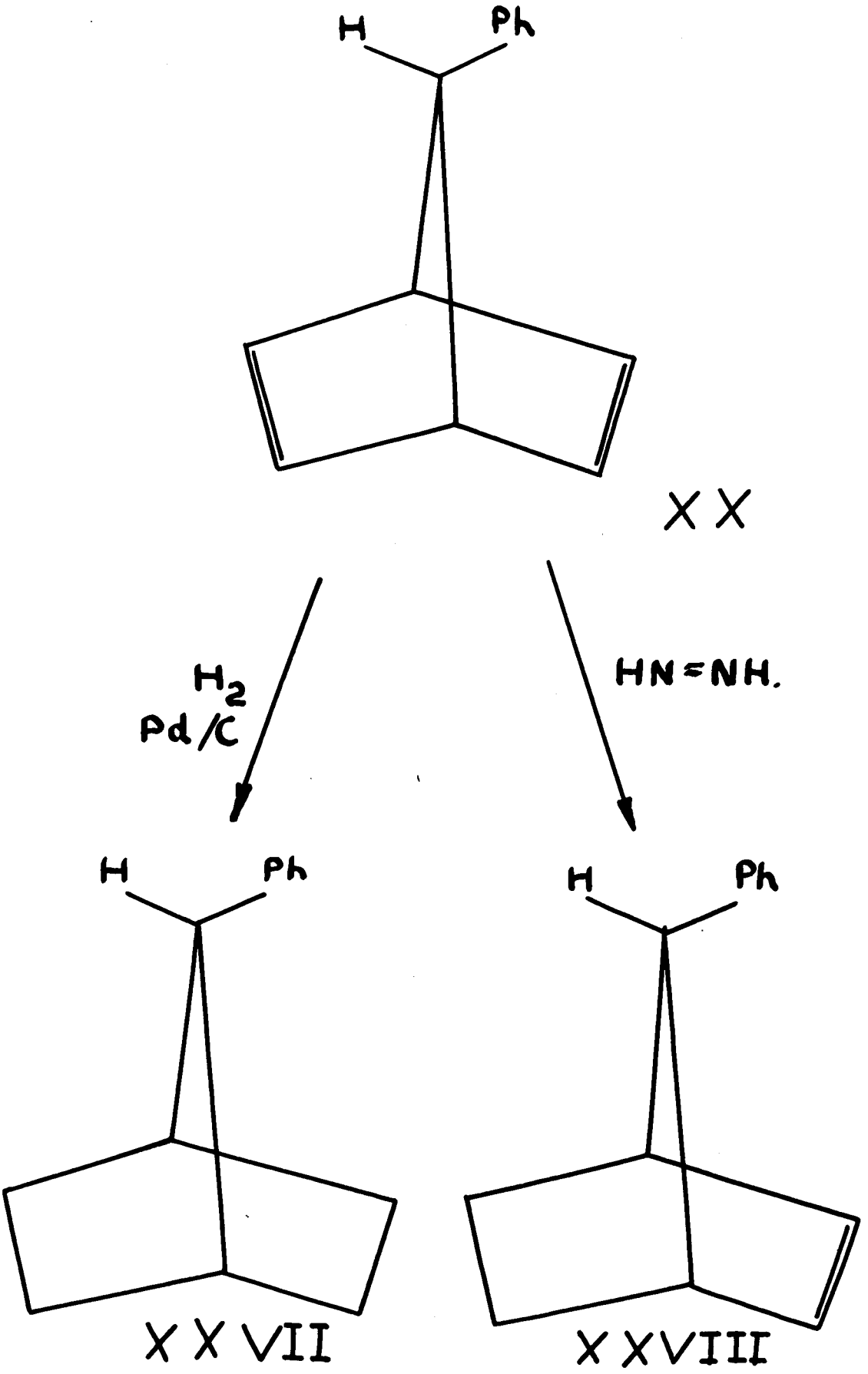
XX

was by treatment of norbornadiene with t-butyl perbenzoate and cuprous bromide to provide a source of t-butoxy radicals. At the time it was believed that the reaction might proceed by anchimerically assisted abstraction of a hydrogen atom to give a delocalized radical of similar structure to the 7-norbornadienyl cation.[39] However, later work with labelled compounds showed[116] that the reaction proceeded via radical addition to the double bonds of the molecule and skeletal rearrangement and so this cannot be claimed as further evidence of electronic delocalization in 7-norbornadienyl compounds. This step offered no practical difficulties.

The next step was replacement of the 7-t-butoxy group by a 7-phenyl group. Story and Fahrenholtz[109] achieved this by refluxing the 7-t-butoxynorbornadiene with phenyl magnesium bromide in benzene. The only modification made was that methyl cyclohexane was used as solvent to raise the reaction temperature and decrease its time. 7-phenylnorbornadiene was formed as the major product but in the final distillation a compound of closely similar boiling point which was judged to be biphenyl was also carried over in appreciable amounts. It was found that pure 7-phenylnorbornadiene could be extracted from the mixture by shaking it briefly with 10% aqueous silver nitrate solution. This was repeated until most of the 7-phenylnorbornadiene had been extracted giving product which was pure by V.P.C. and was used directly for kinetic measurements. The preferential

extraction of 7-phenylnorbornadiene from the mixture was due to a kinetic rather than a thermodynamic effect since if the mixture was shaken with aqueous silver nitrate solution for 30 minutes the proportion of the two olefins in the extract was approximately the same as in the initial mixture. To provide a comparison in this series with a compound in which electronic delocalisation from the 7-position was not possible the 7-phenylnorbornadiene was hydrogenated under mild conditions to give 7-phenylnorbornane. The rate of uptake of hydrogen was closely watched in the hope that hydrogenation of the second double bond would proceed more slowly than the first, enabling 7-phenylnorbornene(XXVIII) to be obtained in a later preparation by stopping the reaction at the appropriate time. No such effect was apparent and 7-phenylnorbornene was prepared by di-imide reduction instead.

Comparison of the rates of di-imide reduction of a series of olefins[117] suggests that the major factor contributing to their differences in reactivity towards this reagent is the amount of strain suffered by the olefinic double bond. The reduction of one double bond of 7-phenylnorbornadiene will certainly lessen the strain on the double bond remaining and so it was hoped that careful control of the reaction conditions might lead to a reaction product in which the norbornene was predominant. The norbornadiene was subjected to di-imide reduction and aliquots withdrawn from the reaction mixture at frequent intervals and examined by V.P.C. to determine the proportions of the starting


H
Ph
XX
H2
Pd/C
HN=NH.
H
Ph
H
Ph
XXVII
XXVIII

material and products.

The reactivity difference was not sufficient to permit complete hydrogenation to the norbornene before appreciable amounts of the norbornane were formed. The reaction mixture containing the greatest proportion of product also contained an equal amount of norbornane and a small amount of unreacted starting material. Fortunately this mixture could be separated without great difficulty by column chromatography and pure norbornene obtained. V.P.C. and N.M.R. spectroscopy of the product indicate that the product consists of only one of the possible pairs of isomers, although an N.M.R. spectrum of the product mixture indicated the presence of the other isomer also comprising probably about 5% of the total yield of norbornenes.

The product is believed to be syn-7-phenylnorbornene.(XXVIII) It would be expected that the anti-double bond, which suffers no steric hindrance from the phenyl group would be more readily hydrogenated by di-imide. In spite of this the reduction of norbornadienes substituted at the 7-position has been observed to occur in the opposite sense giving exclusively the anti-isomers.[118] However, all these compounds had oxygen functions attached to the 7-position and so are poor models for the reduction of 7-phenylnorbornadiene. The vinyl protons of norbornadiene resonate at 3.25τ [123] while those of 7-phenylnorbornadiene resonate at 3.15τ and 3.5τ [109] The introduction of the phenyl group therefore

causes a downfield shift of 0.1τ of one set of vinyl protons and an upfield shift of 0.25τ of the other. It would be expected that the major shift should occur in the resonance of the protons which are **syn** to the phenyl group which suggests that the upfield protons are those **syn** to the phenyl group. It would also be expected that they would be shielded by their proximity to the phenyl group. The high field position of the vinyl protons in the product obtained suggest that they are also **syn** to the phenyl group, particularly since they occur at 4.01τ and those of the small impurity believed to be the other isomer at 3.65τ This difference in chemical shifts is virtually identical with that between the **syn** and **anti** protons of 7-phenyl-norbornadiene.

CHAPTER FOUR

KINETIC MEASUREMENTS

The hydrocarbons prepared as described previously were treated with a solution of potassium t-butoxide in perdeutero-dimethyl sulphoxide. The base solution was standardized by observing the rate at which it catalyzed the isomerization of cyclocta-1,5- diene to cycloocta-1,3-diene. All the kinetic measurements reported here were made using the same base solution in which the half-life of this reaction was 17 minutes unless specifically stated otherwise. After the experiments involving heating the base solution to 110° for long periods the activity of the base solution was checked. In all cases the half-life for the isomerization reaction was found to lie within 20% of the initial value.

Preliminary experiments were conducted by heating stoppered tubes in thermostatted baths and recording their N.M.R. spectra at intervals in order to conserve machine time. Kinetic measurements were made using sealed tubes in a Perkin Elmer Variable Temperature Probe set to the appropriate temperature. Tubes were not removed from the probe during the experiments unless specifically stated. Two experiments were performed under

each set of conditions .

Kinetic Results

7-Phenylnorbornadiene (110°)

In perdeutero-dimethyl sulphoxide the bridgehead protons and the proton at the 7-position fall together to give a three proton multiplet 1.39 ppm. downfield from the resonance of the residual protons in the dimethyl sulphoxide. The relative areas of these peaks were measured repeatedly, both by the integrating device of the N.M.R. machine and by using a planimeter. The machine integral was also used repeatedly to check that the numbers of protons represented by these two peaks was unchanged compared to the phenyl and vinyl protons of the molecule. Performing these measurements suggested that the exchange of 5% of the protons at the 7-position might possibly have been detected and that the exchange of 10% of these protons would definitely have been detected.

No exchange was detected in 12 hours. At the 10% detection limit this indicates a half-life for the exchange reaction of at least 79 hours and at the 10% detection limited of at least 148 hours.

7-Phenylnorbornene (110°)

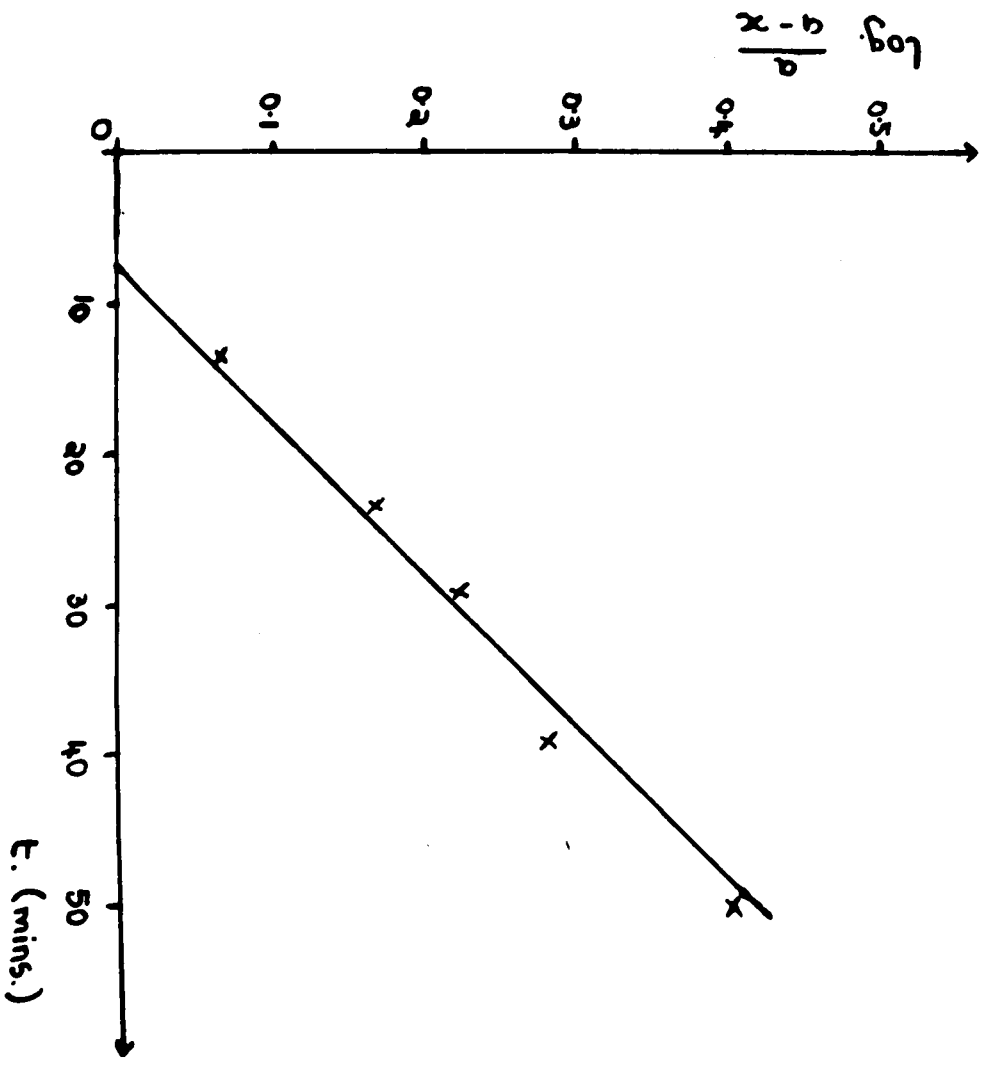
In this case the resonances of the bridgehead protons and the proton at the 7-position appeared separately making the detection of the exchange of 5% of the protons at the 7-position almost certain. Both machine integration and integration by planimeter were used as previously.

No exchange was detected in 12 hours. At the 5% detection limit this indicates a half-life for exchange of at least 148 hours.

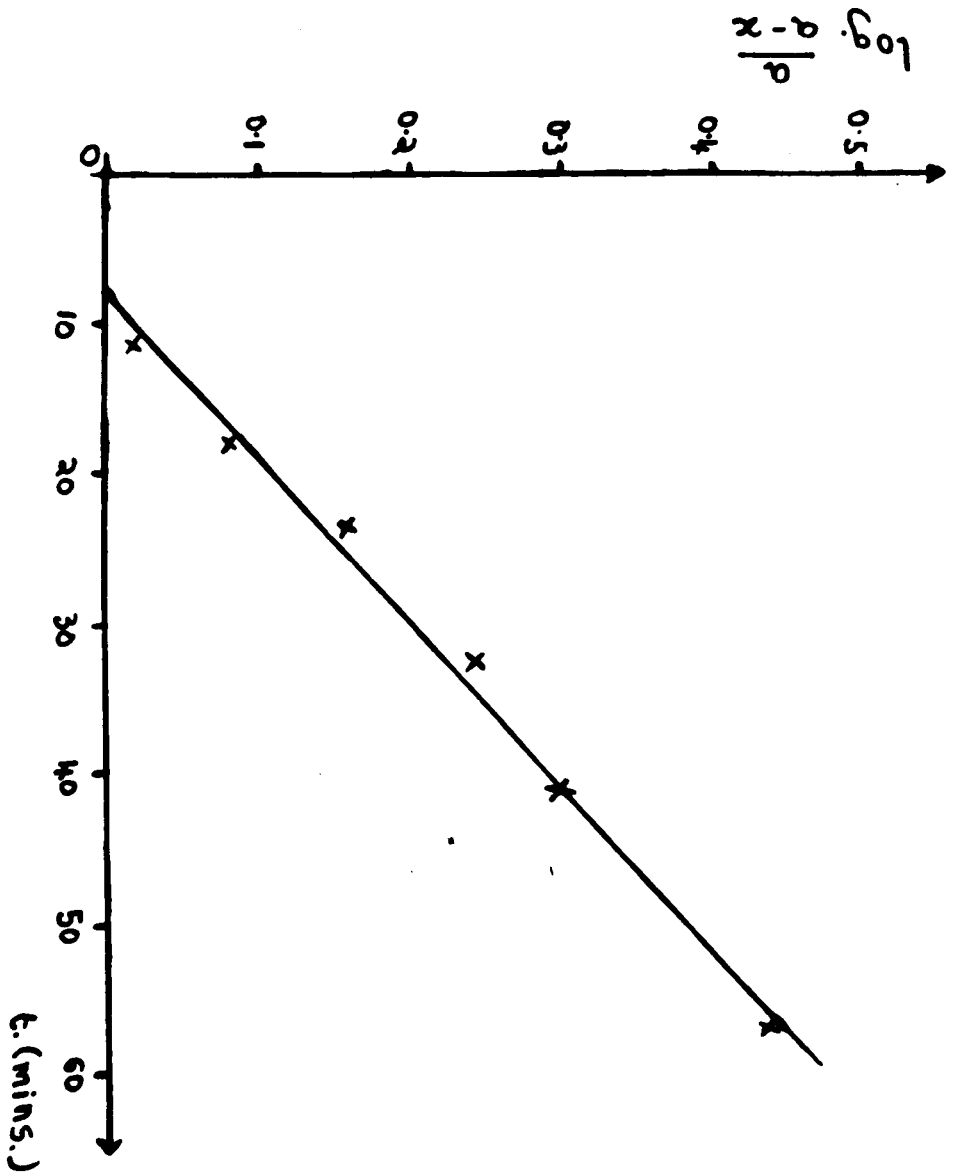
7-Phenylnorbornene (110°)

The benzylic protons appeared downfield and just separated from the peak corresponding to the residual protons of dimethyl sulphoxide. Both machine and planimetric integration were used as previously, planimetric integration to determine the ratio of the protons represented by these two peaks and machine integration to check that protons were not being removed from other parts of the molecule.

The two runs are both tabulated and illustrated graphically to show the correspondence to first order kinetics and the scatter of the points. The intercepts of the graphs are not at zero time because this corresponds to insertion at room temperature.



Exchange of 7-Phenylnorbornane at 110° No. 1



Exchange of 7-Phenylnorbornane at 110° No. 2

RUN NO.1		RUN NO.2	
t (mins)	Benzylic Protons	t(mins)	Benzylic Protons
13.5.	0.86.	11.5.	0.96.
23.5.	0.68.	18.0.	0.83.
29.5.	0.60.	24.5.	0.69.
39.0.	0.52.	32.5.	0.57.
50.0.	0.40.	41.0.	0.50.
		56.5.	0.37.

Half-life = 33 mins. Half-life = 35 mins.

Average Half-life = 34 mins.

7-Phenylnorbornane (65°)

To save machine time the samples were heated in a thermostatted bath (65 ± 0.2°) and removed at inte vals to have their N.M.R. spectra recorded in a normal proton probe at 33.5°. In both cases spectra were run at intervals during the first 24 hours when no exchange could be detected. Approximately one week later a series of spectra were run in a short period of time. The values for exchange given are the average obtained from the series in each case.

RUN NO.1		RUN NO.2	
t(hours)	Benzylic Protons	t(hours)	Benzylic Protons
158.	0.84.	197.	0.75.

These suggest half-lives respectively

Run No.1	632 hours
Run No.2	478 hours.

The mean value is almost precisely 1000 times the half-life at 110°. This suggests an energy of activation for the reaction of approximately 40 K.cals/mole.

Bicyclo(4,2,1) nonatriene

Because of the greater complexity of the resonances of the protons at the 9-position of bicyclo(4,2,1) nonatriene (AB pattern with triplet A part) planimetry could not be used to determine the relative peak areas. Instead machine integration was used. The minimum exchange which could be detected by this means is probably 10%.

No exchange was detected in 24 hours at 110°. This indicates that the half-life for exchange is at least 158 hours.

9-Phenylbicyclo(4,2,1) nonatriene (33.5°)

A preliminary experiment showed that changes occurred in the base solution at 33.5°. Accordingly kinetic experiments were carried out in a normal proton probe.

During the course of the experiment complex changes occurred.

The initial spectrum showed the characteristic singlet and doublet of the starting material 0.25 and 0.48 ppm. respectively downfield from the peak of the residual protons in the dimethyl sulphoxide. During the course of the experiment these three peaks disappeared at an approximately uniform rate and were replaced by what appeared to be a doublet coupled downfield (J=6.8c/s) centre 0.40 ppm. downfield from the residual proton in dimethyl sulphoxide peak. The complexity of this region of the spectrum makes estimation of the rate of this process extremely difficult but the half-life for its occurrence was probably about two hours. It appeared that protons were also being removed at a moderate rate from the diffuse four proton olefinic complex and more slowly from the sharp two proton olefinic complex. After two hours the proton exchanged into the dimethyl sulphoxide corresponded to about 1.1 protons per molecule of 9-phenylbicyclo (4,2,1) nonatriene.

After three days at 33.5° only two peaks were visible in the region immediately downfield from the dimethyl sulphoxide peak. Most of the four proton complex had disappeared and almost half of the two proton complex had also disappeared.

Rather disturbingly, quenching this solution gave what appeared to be mainly starting material, with poor recovery, although the region around 7.0 was complex and ill-defined.

In order to make clearer the nature of the changes occurring in this region of the spectrum a tube was prepared using a fresh batch of base solution made up precisely as previously and taken to Birmingham packed in dry ice in order to observe the spectral changes at 100 Mc/s. It was found that in this case no detectable exchange occurred in six hours. A check on the activity of the base solution showed that the half-life for isomerization of cycloocta-1,5-diene by this batch was approximately 50 minutes.

By the time a further tube was prepared it was found that the starting material had undergone some change. The N.M.R. spectrum showed broad and diffuse absorption. Since the compound was stored in a nitrogen dry-box it is unlikely, although possible, that it suffered oxidation. An alternative possibility is self-addition *via* a Diels-Alder Reaction.

Cumene (65°)

The benzylic proton appears as a heptet which overlaps the dimethyl sulphoxide peak. This made it necessary to estimate the proportion of the benzylic proton at any time by comparing the height of the central peak of the heptet and that of the peak corresponding to the phenyl protons. Because of the lesser accuracy of this method, as compared to integration either by planimeter or machine three kinetic measurements were made.

RUN NO.1

t(mins)	Benzylic Protons
16.0.	0.96.
24.5.	0.86.
39.0.	0.77.
50.0.	0.69.
70.0.	0.63.

Half-life = 108 mins.

RUN NO.2

t(mins)	Benzylic Protons
13.0.	0.93.
27.0.	0.84.
42.0.	0.82.
60.5.	0.72.
82.0.	0.67.
100.5.	0.62.

Half-life = 132 mins.

RUN NO.3.

t(mins.)	Benzylic Protons.
22.	0.94.
41.	0.88.
54.	0.75.
70.	0.65.
88.	0.59.

Half-life = 126 mins.

Average half-life = 122 mins.

Discussion of Kinetic Measurements

Two preliminary points emerge from the kinetic measurements. First, the rates of exchange are highly dependent on the activity of the base solution. This is made clear by the complete failure of 9-phenylbicyclo (4,2,1) nonatriene to react in sixhours, using base solution which had a half-life for isomerisation of cycloocta-1,5- diene of about 50 minutes, while using base solution of half-life 17 minutes, complex and extensive changes occurred in two hours at the same temperature. Comparisons of the rates of exchange can only properly be made if the base solution used to effect exchange is from the same stock. In all the cases compared here this was the case.

Secondly, the decision to synthesize phenyl-substituted starting materials is confirmed. Even with phenyl substitution detectable exchange could not be observed with 7-phenylnorbornadiene and the 7-phenylnorbornene, assigned the syn stereochemistry. The labilizing effect of phenyl substitution is illustrated by the difference in reactivities of bicyclo (4,2,1) nonatriene and 9-phenylbicyclo (4,2,1) nonatriene. Without phenyl substitution it is certain that exchange could not have been observed in any of the compounds studied.

For a definite statement to be made as to whether non-classical interactions occur in the carbanions studied one of two conditions must apply. Either the differences in rates of exchange between the compounds must be so great as to make impossible their attainments by any combination of the factors operating other than non-classical electron delocalization, or, if the rate differences are not of this high magnitude, the nature and magnitudes of the factors other than electron delocalization must be accurately known.

Unfortunately in the case of this work neither of these conditions applied. In an effort to obtain a case for comparison, the rate of exchange of the benzylic hydrogen atom of cumene was measured. In this compound the only effects operating are those of conjugation, which tends to create a planar carbanion, and the opposing increased stability of carbanions as the negative charge occupies an orbital with high s-character tending to keep the carbanion tetrahedral. The relative magnitudes of these effects and the balance struck between them in acyclic systems is not accurately known.

In addition to these effects, the tendency of the bicyclic carbanions to assume a planar configuration will be further restrained by the increase in strain energy of the molecules which this would cause. If it is assumed that the combination of strain and s-character effects overwhelms the tendency of conjugation to produce a planar carbanion, thus causing the geometry of the carbanion to be close to that of the starting molecules, little

difference would be expected in the rates of exchange of norbornane, norbornene and norbornadiene derivatives. X-ray and electron diffraction studies[124-126] have shown that the angle of the bridge bonds at the 7-position in these three types of compounds is essentially the same, falling in the range 96-98°. In fact the observations on the bicyclo (2,2,1) compounds show that at 65° the rate of exchange of ~~7-phenyl norbornadiene~~ cumene is approximately 250 times that of ~~cumene~~ 7-phenylnorbornane and that at 110° 7-phenylnorbornene (syn- isomer) and 7-phenylnorbornadiene undergo exchange at rates which are at least 260 and 140 times slower respectively than that of 7-phenylnorbornane. These rate differences are not sufficient to permit any definite statement to be made, the limiting factor in setting the limits being the durability of the base solution. If they are due to the increased strain energy that would attend any movement towards a planar carbanion on moving from a norbornane to a norbornadiene derivative it is somewhat surprising that the effect of introduction of a single double bond into the already strained norbornane skeleton (with probably a very small effect on the geometry of the carbon atom to which the proton removed is attached) should produce a greater effect than the transition from the acyclic cumene to the highly strained norbornane. It is possible that the fact that the carbon atoms attached to the carbanion centre in cumene are primary whereas in the bicyclo (2,2,1) compounds they are tertiary may have some effect but this should only be of the second order and its nature is difficult to see. The evidence

available suggests that the energy of activation for the exchange reaction of 7-phenylnorbornane is approximately 40 K.cal/mole though because of the scarcity of data available it may possibly lie within ± 5 K.cals of this value. Values are not available for other compounds which would make meaningful comparisons possible. All that can be said is that it is considerably higher than the value of 18.0 ± 0.2 K.cals found for toluene[81] as would be expected for the formation of a tertiary carbanion in which conjugation involves an increase in strain energy as compared to an acyclic primary carbanion. The figures obtained agree with the proposal that in the norbornene and norbornadiene derivatives formation of a carbanion involves a destabilizing 4π-electron interaction with the electrons of the anti - double bond similar to the stabilizing 2π- electron interaction in the 7-norbornadienyl and anti - 7 - norbornenyl cations. An alternative possibility is that in the case of the 7-phenylnorbornadienyl anion a destabilizing 6π- electron interaction occurs as predicted by Goldstein[43] who suggested that this anion would be destabilized and antibicycloaromatic. They do not, compel the acceptance of either of these proposals.

The lack of precise knowledge of the nature of the changes occurring when 9-phenylbicyclo (4,2,1) nonatriene was treated with the base solution is unfortunate. Certain conclusions, however, are possible. The rate of the changes occurring to the peaks representing the bridgehead and benzylic protons and the rate of loss of protons from each of the two sets of vinyl protons are

different and therefore probably occur by unrelated mechanisms. Had observation of the changes occurring in the region of the bridgehead and benzylic protons at 100 Mc/s. been possible it would have been most valuable. Besides spreading out a rather crowded region, in conjunction with observations at 60 Mc/s, it would have determined whether the two protons appearing constituted a doublet or two singlets. The close correspondence of the separation of these two peaks (6.8 c/s) to the coupling constant of the doublet representing the bridgehead protons of the starting material (J=6.5 c/s.) suggests that these peaks are a doublet, representing bridgehead protons in a closely similar molecule. The most tempting explanation of this is that the molecule is undergoing exchange with inversion of configuration at the 9-position; possibly to exchange a favourable 6_{π}-electron interaction for an unfavourable 4_{π}-electron interaction. Against this is the fact that the two peaks showed no signs of collapsing to a singlet after three days when an appreciable proportion of the vinyl protons with which coupling would be required had been exchanged for deuterium. The data available is insufficient to permit the solution of the problem but it seems reasonable to say that in 9-phenylbicyclononatriene a process of approximate half-life 2 hours at 33.5° is occurring which almost certainly involves the removal of a proton from the 9-position.

Unless secondary effects associated with the structural differences between cumene and the bicyclic compounds are large this would be unexpected. If the rates of exchange of 9-phenylnorbornene

and 7-phenylnorbornadiene are less than that of 7-phenylnorbornane simply because increased angle strain robs these carbanions of some of the conjugative stabilization available to 7-phenylnorbornane it would be expected that exchange of protons from 9-phenylbicyclo (4,2,1) nonatriene would be intermediate in rate between the values for cumene and 7-phenylnorbornane. In fact it appears that the benzylic proton may be removed more easily from 9-phenylbicyclo (4,2,1) nonatriene than cumene. A rationalization of this fact is provided by Goldstein's prediction that this anion will be stabilized and bicycloaromatic. If, in fact, electronic stabilization is occurring in this system it will be far easier to detect by further experiments than the electronic destabilization which may occur in the (2,2,1) series. Hydrogenation of the double bonds of the bicyclo (2,2,1) compounds lessens the strain in the molecule and so on the basis of both of strain effects and electronic effects an increase in rate of exchange on hydrogenation to the norbornane derivative would be expected. A distinction could only be made on the basis of the magnitude of the change involved, which is difficult in the absence of a large body of related work.

If stabilizing electron delocalization is present in the anion derived from 9-phenylbicyclo (4,2,1) nonatriene hydrogenation to the bicyclononane would cause diminution of the rate of exchange

whereas if only strain effects were important it should cause increase in the rate of exchange by allowing a closer approach to conjugation of the anion formed. This distinction will be easier to make. Also, if electronic effects are found to occur, reduction by di-imide to 9-phenylbicyclo (4,2,1) nona-2,4-diene will almost certainly occur with greater specificity than is the case for the mono-reduction of 7-phenylnorbornadiene. This mono-reduced compound will permit greater precision in the determination of the nature of any electronic effects operating.

In summary it seems that the data obtained tempt, though do not substantiate speculation. The synthesis of 9-phenylbicyclo (4,2,1) nonatriene paves the way to experiments which may prove definitive.

EXPERIMENTAL

INTRODUCTION

Melting Points were determined on a Kofler heated stage apparatus and are given uncorrected.

I.R. Spectra were recorded on Perkin Elmer 237 and 257 instruments.

U.V. Spectra were recorded using a Unicam SP 800 spectrophotometer. Extinction coefficients were determined using a Unicam SP 500 series 2 spectrophotometer.

N.M.R. Spectra were recorded on a Perkin Elmer R 10 instrument operating at 60 Mc./s.

G.L.C. was carried out using an F&M model 720 instrument with a thermal conductivity detector with columns as indicated in the text.

T.L.C. plates were made up from either Kieselgel G. (Macherey, Nagel & Co.) or Aluminium Oxide G. (Merck A.G.) as indicated.

Column Chromatography was carried out using B.D.H. Silica Gel for Column Chromatography.

Light Petroleum refers to the fraction boiling in the range 30° - 40°.

Petroleum Ether refers to the fraction boiling in the range 40° - 60°.

Cyclooctatetraene was freshly distilled before use at approximately 100mm. pressure.

Tetrahydrofuran was distilled from lithium aluminium hydride under an atmosphere of nitrogen and stored over molecular sieve type 4A.

Dimethyl Sulphoxide was distilled from sodium hydride under high vacuum and stored over molecular sieve type 4A.

Perdeutero-Dimethyl Sulphoxide was supplied by Ciba and stood over molecular sieve type 4A in a nitrogen dry box before use.

Diglyme was distilled from lithium aluminium hydride under high vacuum and stored over molecular sieve type 4A.

Acetonitrile was distilled from phosphorus pentoxide and stored over molecular sieve type 4A.

Anhydrous ammonia was obtained by distilling liquid ammonia supplied by I.C.I. Ltd. from sodium into the reaction flask immediately before use.

Benzene sulphonyl hydrazide consisted of Genitrom B.S.H. powder (Fisons Industrial Chemicals Ltd.) recrystallized rapidly from methanol and dried under vacuum over phosphorus pentoxide.

Pure dry nitrogen was the normal bench supply passed successively through Fieser's solution, conc. sulphuric acid and solid potassium hydroxide pellets.

Lithium methoxide was prepared by dissolving chips of freshly cut lithium in A.R. methanol under an atmosphere of pure dry nitrogen. Excess methanol was removed under reduced pressure and the resulting solid subjected to a vacuum of approximately 0.1mm.

ATTEMPTED SYNTHESIS OF 9-PHENYLBICYCLO (4,2,1) NONATRIENE

A. Via Ester Cleavage

Attempted preparation of 9-benzoyloxy-9-Phenylbicyclo (4,2,1) nonatriene

As indicated by Cantrell and Shechter [75]

Dilithium cyclooctatetraenide was made by a method similar to that of Katz and Garratt.[93]

Lithium (3.5g., 0.50 mole) was added in small, freshly-cut, chips to dry tetrahydrofuran (200ml.) maintained at 0° under an atomosphere of pure, dry nitrogen. The mixture was stirred vigorously and freshly distilled cyclooctatetraene (26g., 0.25 mole) was added. The reaction mixture was maintained at 0° under nitrogen and vigorous stirring continued. After one hour the initial pale-yellow colour had changed to dark green and only a few small pieces of lithium could be seen. After a further hour no pieces of solid lithium could be seen. Benzoyl chloride (77g., 0.55 mole) was added over a period of 15 minutes, causing the formation of an orange-yellow precipitate. The reaction mixture was allowed to warm to room temperature; distilled water was then added until the total volume was 1000 ml. The aqueous suspension was extracted with carbon tetrachloride (3x200 ml), and the carbon tetrachloride extracts combined and washed with dilute sodium carbonate solution (2x200 ml), and water (2x200 ml), and dried over magnesium

sulphate. Removal of the solvent under reduced pressure gave a deep orange, highly viscous oil (47.0g.).

This oil was dissolved in the least possible amount of carbon tetrachloride and petroleum ether was added in small portions. The precipitates produced were divided into three major fractions;

1) An orange oil (11.1g.).

2) A yellowish-brown tarry solid (27.6g.).

3) A brown resin (7.2g.).

Attempts to obtain solid material from fraction 1 by trituration with petroleum ether and by recrystallization at acetone-dry ice temperature from various petroleum ether - ether and petroleum ether - methylene chloride mixtures failed. This fraction was discarded.

Fraction 3 was completely insoluble in petroleum ether and benzene, very sparingly soluble incarbon tetrachloride, and readily soluble in methylene chloride and acetone. Solutions in methylene chloride and acetone to which less polar solvents were added deposited unchanged resinous material, as did attempts at low temperature recrystallization. This fraction was also discarded.

Trituration of fraction 2 with petroleum ether and fractional crystallization from petroleum ether - methylene chloride mixtures at low temperature caused some initial improvement in appearance by removing portions of both oil and resin and

gave a yellow granular solid which could not be improved by further fractional crystallization. Chromatography of a small amount of this material on a column of silica gel using eluents of increasing polarity, until a 10% V/V solution of methylene chloride in ether was reached, eluted material of essentially the same composition as starting material.

An I.R. spectrum showed a weak band at ν= 1778 corresponding to benzoyl chloride. The remainder of fraction 2 was subjected to a high vacuum for 24 hours at room temperature and the yellow granular solid remaining (23.6 g) used as a basis for further experiments.

Melting Range	105 - 120°
ν (Nujol Mull)	3040(m),3010(s),1718(s), 1605(m),1580(m),1285(vs), 1240(s),1111(m),
u.v. (ethanol)	End absorption with shoulder tailing away to 280 m_μ
$\tau(CCl_4)$	1.85 - 2.78 (complex) 10H, 3.93 (multiplet) 4H, 4.71 (multiplet) 2H, 6.05 - 6.25 (multiplet) 2H.

The properties of authentic material are[94]

M. Pt.	123-124°
ν	1715(s), 1603(m), 1580(m) 1285(vs), 1235(s), 1115(s), 1030(m), 694(s).
λ_{max}	266 (2900), 258 (3050), 244 (11,800).
τ	1.8 - 2.9 (multiplet) 10H, 3.92 (multiplet) 4H, 4.69 (multiplet) 2H? 6.16 (broad multiplet) 2H.

Modifications

Several modifications were made to the procedure described above in an attempt to improve the product. Reactions were carried out on a smaller scale (0.10 mole lithium) in which;

a) The lithium-cyclooctatetraene mixture was stirred at 0° for 12 hours to ensure the complete formation of dilithium cyclooctatetraenide.

b) The ratio of benzoyl chloride to cyclooctatetraene was reduced to exactly 2:1.

c) Both the preceding changes were made and the dilithium cyclooctatetraenide solution was added to the benzoyl chloride rather than vice versa.

None of these modifications produced a more tractable product than the original method.

Attempted preparation of 9-Phenylbicyclo (4.2.1) nonatriene-9-ol.

Lithium (0.7g.,0.10 mole) was added in small, freshly-cut, chips to dry tetrahydrofuran (50 ml.) maintained at 0° under an atmosphere of pure dry nitrogen. Freshly distilled cyclooctatetraene (5.2g. 0.05 mole) was added and stirred vigorously for two hours. Benzoyl chloride (7.0g, 0.05 mole) dissolved in dry tetrahydrofuran (50 ml) was added over a period of one hour, with vigorous stirring. During this time the reaction mixture changed from a deep green solution to a yellow-brown suspension. The reaction mixture was diluted to 600 ml. with distilled water and extracted with carbon tetrachloride. (3x100ml). The combined carbon tetrachloride extracts were washed with water (2x100 ml) and dried over magnesium sulphate. The bulk of the extract was reduced to 20 ml. and petroleum ether added in small portions until no further precipitation occurred. The precipitate was filtered off, washed with a little ice-cold ether and dried under vacuum giving a yellow brown solid (8.2g).

Melting Range	100 - 125°
" (Nujol mull)	3700 - 3100 (vs, broad).
	No absorption 1700 - 1800

Attempts to purify the product by recrystallization and column chromatography caused no significant improvement in the product.

Attempted Extraction of 9-Phenylbicyclo (4.2.1) nonatriene-9-ol.

The product of the previous preparation was dissolved in carbon tetrachloride (500 ml), excess phthalic anhydride (10g.) added and the reaction mixture heated under reflux for 8 hours. It was allowed to cool and washed with dilute sodium carbonate (3x200ml).

The sodium carbonate washings were acidified with dilute hydrochloric acid and extracted with ether (3x200ml). The combined ethereal extract was dried over magnesium sulphate. Evaporation of the solvent gave only a few traces of solid material which showed general, diffuse absorption in the I.R. spectrum.

Reduction of the crude 9-Benzoyloxy-9-phenylbicyclo (4,2,1) Nonatriene

Freshly cut lithium (28 mg., 2 mol.) was dissolved in anhydrous ammonia (50 ml) kept at reflux by an acetone - dry ice condenser. A solution of crude 9-benzoyloxy-9-phenylbicyclononatriene, melting range 105-120° (628 mg., 1 mol.), in a mixture of tetrahydrofuran (4.0 ml) and methanol (1.0 ml.) was added in one portion with vigorous stirring producing a deep red colour which quickly faded to red-brown. The reaction mixture was stirred for a further five minutes and then distilled water was cautiously added until the volume reached 150 ml. The aqueous suspension was extracted with n-pentane (4 x 50 ml.) and the pentane extracts combined and washed with water (2 x 50 ml.) and dried over magnesium sulphate. Removal of the solvent gave a yellow amorphous solid (235 mg). The product had a poorly characterized I.R. spectrum which appeared to be a combination of the spectra of starting material and 9-phenylbicyclo (4,2,1) nonatriene-9-ol

T.L.C. of the product (silica gel plates; eluent, benzene) showed spots,

R_F	0.0	0.20	0.38

The spot at R_F 0.38 corresponds to the major product of the attempted preparation of 9-benzoyloxy-9-phenylbicyclo (4,2,1) nonatriene and that at R_F 0.20 to the major product of the attempted preparation of 9-phenylbicyclo (4,2,1) nonatriene-9-ol.

Further extraction of the reaction mixture with ether (4x50 ml) gave more product of essentially the same composition (247 mg.).

B.Via Organometallic Compounds.

9-Phenylbicyclo (6,1,0) nonatriene

Modified method of Katz and Garratt.[93]

Freshly cut chips of lithium (650 mg., 2 mol) were dissolved in anhydrous ammonia (200 ml.) which was maintained under reflux by an acetone- dry ice condenser and vigorously stirred. A solution of freshly distilled cyclooctatetraene (5.0 g., 1 mol.) in dry tetrahydrofuran (30 ml.) was added over 15 minutes to give a deep orange solution and a yellow precipitate. Stirring was continued and benzal chloride (7.50 g., 1 mol) dissolved in dry tetrahydrofuran (30 ml.) was added over 15 minutes to give a deep emerald green solution which changed to a yellow-brown suspension in a further 20 minutes. Stirring was suspended and distilled water (1000 ml.) was cautiously added, producing a bright orange, oily suspension. The aqueous suspension was extracted with n-pentane (4x200 ml.) The combined pentane extracts were washed

with water (4x200 ml.) and dried over magnesium sulphate. Removal of the solvent gave a deep orange oil (9.0g.) which could not be caused to crystallize. T.L.C. of this product (alumina; eluent, n-pentane) showed a large number of definite spots and indistinct streaks. The oil was dissolved in the minimum volume of petroleum ether, applied to a column of activated alumina (100g.) and eluted with petroleum ether (500 ml.) The solvent was removed from the eluate under reduced pressure to give a yellow brown tarry solid (7.9g.). T.L.C. of this product (alumina; eluent, n-pentane) showed a major spot, R_F 0.0, three or four indistinct streaks in the range R_F 0.0 to R_F 0.15 and a major spot R_F 0.26. Recrystallization from methanol with the use of activated charcoal gave pale yellow plates,

M.Pt 57 - 59° (2.2g., 23% theoretical yield)

A small portion was recrystallized from methanol twice more to give

<u>syn-9-phenylbicyclo (6.1.0) nonatriene.</u>

M. Pt.	60.5°
ν (Nujol mull)	3057(w), 3028(m), 1606(m), 1495(m), 685 (s).
U.V.	End absorption with a shoulder ending at 290
τ (CCl_4)	2.48 - 2.97 (multiplet) 5H, 3.51 - 4.19 (overlapping multiplets) 6H. 8.10 (doublet, J = 6.5 c/s.) 2H, 8.51 (triplet, J = 6.5 c/s) 1H
Analysis	Found : C,92,5; H,7.55
	$C_{15}H_{14}$ requires C,92.7; H,7.3%

Thermal Rearrangement.

syn-9-phenylbicyclo (6,1.0) nonatriene (10mg.) was dissolved in di-n-butyl ether (20ml) and the solution heated under reflux. Aliquots were removed at hourly intervals. Their u.v. spectra changed from a rounded shoulder to a straighter and more elongated shoulder over a period of four hours and after this time no further change occurred.

Attempted Preparation of Tricarbonyl (diglyme) molybdenum(0)

Method of Coffield and Werner[95]

Molybdenum hexacarbonyl (3.0g) was added to a mixture of diglyme (10.0ml) and benzene (3.0ml) under an atmosphere of pure dry nitrogen and heated under reflux on an oil bath. Aliquots were withdrawn and their I.R. spectra examined after 4,8,12 and 24 hours. None showed any absorption bands in the range ν = 2200 - 1800 other than that due to molybednum hexacarbonyl. The I.R. of tricarbonyl (diglyme) molybdenum(0) has[95]

ν 1905 (s,broad) 1835 (s,broad).

Modifications

Toluene was substituted for benzene in the above reaction mixture. After four hours the reaction mixture showed none of the I.R. bands on the desired product. After 16 hours the reaction mixture had become a dirty brown colour and a large amount of metallic molybdenum had been deposited.

In an attempt to monitor the reaction more closely an apparatus was constructed in which the carbon monoxide evolved was collected over water. About a third of the stoichiometric volume of carbon monoxide was evolved in nine hours by which time the reaction mixture was heavily discoloured and grains of metallic molybdenum had been precipitated. An I.R. spectrum at this stage showed none of the bands corresponding to product.

A reaction mixture of the initial composition including benzene was placed in a sealed tube and heated at 120° for four hours. After this time no product had been formed.

Tricarbonyltris(acetonitrile)molybdenum(0)

Method of Tate, Knipple and Augl.[96]

A mixture of molybdenum hexacarbonyl (5.0g) and acetonitrile (30ml.) was heated in a fume cupboard under reflux, on an oil bath, while a very slow stream of pure dry nitrogen played on its surface. At intervals of approximately one hour sufficient fresh acetonitrile to maintain the bulk of the reaction mixture was added in such a way as to wash molybdenum hexacarbonyl which had sublimed into the condenser back into the reaction flask. After four hours the solution had become a clear golden yellow and molybdenum hexacarbonyl had ceased to sublime out. After six hours heating was stopped and the nitrogen flow increased. After 12 hours the acetonitrile had evaporated leaving a yellow crystalline solid (5.85g., 102% theoretical yield).

" (Nujol mull) 1912(s), 1784(s).

Authentic material has,[97]

" (Nujol mull) 1915(s), 1783(s).

Attempted Preparation of Tricarbonyltris (tetrahydrofuran) molybdenum(0)

Tricarbonyltris (acetonitrile) molybdenum(0), (250mg.) was added to dry tetrahydrofuran (1.0ml) cooled to 0° under a nitrogen atmosphere. The reaction mixture was kept at 0° for several hours but no precipitate formed. The reaction mixture was allowed to warm to room temperature and left to stand. Portions were extracted at intervals and their I.R. spectra examined in the range ν = 2,200 - 1,800. At no time did bands corresponding to the formation of a new complex appear. After approximately one week the reaction mixture had changed into a very fine blue suspension.

Reaction mixtures of the same composition were made up and warmed at different temperatures for different lengths of time. All ultimately formed a blue suspension as inthe previous case except for a reaction mixture heated to 65° for 30 minutes This assumed a permanent brown colour and had I.R. bands.

ν 1780(s) 1721(s).

The preceding series of reactions were carried out using reaction mixtures to which syn-9-phenylbicyclo (6,1,0) nonatriene

had been added.

The results were exactly as previously.

Tricarbonyl (syn-9-phenylbicyclo (6,1,0)nonatriene)molybdenum(0)

To tricarbonyltris (acetonitrile) molybdenum(0) prepared *in situ* from molybdenium hexacarbonyl (5.0g., 1 mol.) as previously under a slow stream of pure dry nitrogen, were added cyclohexane (50ml.) and syn-9-phenylbicyclo (6,1,0) nonatriene (3.68g., 1 mol.). The reaction mixture was heated under reflux. Aliquots were removed at intervals by syringe through a serum cap and their I.R. spectra examined. After six hours the bands due to the initial molybdenium complex had disappeared. Heating was stopped and the nitrogen flow increased. After six hours all the cyclohexane had evaporated leaving a red-brown solid. The flask was removed to a nitrogen dry box and further manipulations carried out there. A nujol mull of the product showed seven or eight major and minor bands in the range V = 2,200 - 1800. The total solid was transferred to a Soxhlet thimble and then removed from the dry box to be extracted with cyclohexane (20ml.) for six hours. The extract was transferred back to the dry box and the isolation of product carried out there. The reaction solution was allowed to cool to room temperature when crystals were deposited. These were filtered off on a sintered crucible and dried by exposure to a stream of pure dry nitrogen, to give dark red shining plates of tricarbonyl (syn-9-phenylbicyclo(6,1,0) nonatriene molybdenum(0)

M.Pt.	140-145 (decomposes)
ν(cyclohexane)	2003(s), 1939(s), 1919(s). 1602(w)
λ_{max} cyclohexane	326 (10,500)

τ (CCl_4)	2.52 - 3.11 (multiplet) 5H, 3.85 - 4.15 (multiplet) 2H, 4.41 - 4.89 (multiplet) 2H, 5.23 (broad doublet, J ≈ 10.5 c/s) 2H, 8.08 (triplet, J = 6.0 c/s) 1H, 8.60 (doublet, J = 6.0 c/s) 2H.
Analysis	Found : C 57.4; H, 3.85; Mo, 25.8
	$C_{18}H_{14}O_3Mo$ requires C, 57.8; H, 3.75; Mo, 25.6%

A few crystals of the complex were dissolved in ether and the olefin displaced by the method of Grimme[98]. The ethereal solution was decanted and washed three times with dilute acetic acid and twice with water. It was then dried over magnesium sulphate. The ether was removed by evaporation and the residue dissolved in cyclohexane. The u.v. spectrum of this solution was identical with that of a cyclohexane solution of syn-9-phenylbicyclo (6,1,0) nonatriene .

Petroleum Ether (low in Aromatics)

Petroleum ether, boiling range 120-160° (Hopkin and Williams G.P.R.) was shaken overnight with an equal volume of nitrating mixture; composition by weight, 58% conc. sulphuric acid, 25% conc.

nitric acid, 17% distilled water, as described by Tongberg and Johnson.[99] The hydrocarbon layer was separated and washed with conc. sulphuric acid until the washings were colourless and then with water. This procedure was repeated twice. The hydrocarbon layer was dried over magnesium sulphate and fractionally distilled. The fractions collected covered 5° boiling ranges from a first fraction boiling range 120-125° to a last fraction of boiling range 155-160°. These fractions were stored over molecular sieve type 4A, before use. All showed absorption maxima at 260mμ. The maximum optical density of any fraction in a 1cm. cell using air as reference at 260mμ was 0.6 and that of the fraction boiling range 155-160° was 0.3.

Attempted Thermal Rearrangement of Tricarbonyl (syn-9-phenylbicyclo (6,1,0)nonatriene) molybdenum(0)

Tricarbonyl (syn-9-phenylbicyclo(6,1,0)nonatriene)molybdenum(0) (20mg) was added to petroleum ether (3.0ml) boiling range 155-160° (low in aromatics). A stream of pure dry nitrogen was passed over the surface of the reaction mixture for several minutes before heating commenced. The reaction mixture was heated on an oil bath which was in the temperature range 155-157° throughout. Samples were withdrawn through a serum cap and their I.R. spectra examined in the range ν = 2,200 - 1,800 (Perkin-Elmer 457, 0.25mm cells, scale expansion x 2½).

The appearance of the solution and the I.R. changed as follows;

30 minutes — Appearance, No change.
I.R. Shoulders ν = 1985, 1892, broadening of major peaks (2003, 1939, 1919).

60 minutes — Appearance, Slight darkening.
I.R. Peak at 1985, shoulders at 1991, 1892, 1878.

90 minutes — Appearance, definite darkening of solution
I.R. Peak at 1985 increases also peaks at 1991 and 1878, shoulders at 1971, 2014 .

120 minutes — Appearance, Dark brown with black granular precipitate. I.R. All previous peaks increase slowly except ν = 1991 which increases rapidly.

150 minutes — Appearance, No change in colour, increase in amount of black precipitate.
I.R. Peak at 1991 increases again, others remain approximately the same.

180 minutes — Appearance, colour somewhat paler, dark precipitate increases
I.R. Approximately two thirds of starting material have gone. Peak at 1991 is by far the strongest, all others have declined in intensity

The peak at ν = 1991 corresponds to molybdenum hexacarbonyl. The black granular precipitate was filtered off and identified as metallic molybdenum. The solution was evaporated to dryness to give a dark brown sludge from which molybdenum hexacarbonyl could be

sublimed easily. Olefins were displaced and extracted from this portion by the method of Grimme[98] T.L.C. (Alumina; eluent, n-pentane) indicated a complex mixture of products.

Synthesis of 9-Phenylbicyclo(4.2.1) nonatriene.

β- Methoxystyrene

Modified method of Miller.[100]

A slow stream of pure dry nitrogen was passed over the surface of methanol (A.R., 500 ml.) for approximately half an hour. Sodium (23.1g.) was added in small quantities while the reaction mixture was cooled on an ice bath. After all the sodium had dissolved phenylacetylene (46.5g) and pure dry dimethyl sulphoxide (100ml.) were added and the mixture heated under reflux under as slow a stream of nitrogen as possible. Aliquots were withdrawn at intervals through a serum cap. They were poured into water and the aqueous mixture extracted with n-pentane. The pentane extracts were washed three times with water to remove dimethyl sulphoxide and dried over magnesium sulphate. The progress of the reaction was followed by observing the disappearance of the band at ν = 2115 (phenylacetylene) and the appearance of the band at ν = 1650 (β -methoxy styrene) in the I.R. spectra of these extracts. After 28 hours the reaction appeared to have gone to completion and the reaction mixture was allowed to cool to room temperature. Distilled water (1000 ml) was added and the aqueous suspension extracted with n-pentane (4 x 300 ml.) The combined pentane extracts were washed with water (4 x 300 ml.) and dried over magnesium sulphate. Removal of the solvent under reduced pressure gave a dark brown liquid (34.2g). Distillation under reduced pressure gave two colourless fractions.

1. Phenylacetylene, B.Pt. 50° at 50mm (7.9g., 17% recovery).

2. β-methoxystyrene, B.Pt. 89° at 8mm., lit.value.[101] 99° at 13mm. (22.8g., 37% theoretical yield).

I.R. Identical with β-methoxystyrene (high boiling) obtained by Miller.[100]

λ_{max} 262 (4750) 272 (3400, shoulder)

$\tau(CCl_4)$ 2.31 - 2.88 (complex multiplet) 5H,
4.00 (doublet J = 7.2 c/s) 1H,
4.85 (doublet J = 7.2 c/s) 1H,
6.38 (singlet) 3H.

n^{25}_D 1.5628.

Lit values; Miller[100] n^{20}_D 1.5683
Auwers[101] n^{20}_D 1.5639

Tropylium Fluoroborate

Tropylium fluoroborate was prepared from phosphorus pentachloride (300g.) by the method of Conrow[102] Yield, 81g. (lit yield, 102-114g).

α-Phenyl-α-(7-tropyl) acetaldehyde

Method of Vol'pin, Akhrem and Kursanov[103]

β-methoxystyrene (53.6g., 1 mol) was dissolved in methanol (1600ml.) and distilled water (400ml.) added. Tropylium fluoroborate (71.2g., 1 mol) was then added and the mixture vigorously stirred. Some of the tropylium salt dissolved immediately giving the solution a red colour. After 30 minutes all the tropylium salt had dissolved and the reaction mixture had

become yellow. Distilled water (300ml.) was added and the mixture extracted with n-pentane (6x600ml.) The combined pentane extracts were washed with water (6x600ml.) and dried over magnesium sulphate. Removal of the solvent gave a viscous yellow oil (89g.). This was dissolved in the minimum amount of petroleum ether (total volume 200ml.) and cooled to 0°. Yellow crystals (9.0g.) were precipitated and separated by filtration. Concentration of the remaining solution gave only a viscous yellow oil. An I.R. spectrum showed strong absorption in the range ν =1050-1200. The residue was taken up in a mixture of hydrochloric acid (1N,300ml.) and dioxan (300ml.) and heated on an oil bath at 65° for four hours. After this time the reaction mixture showed no absorption in the range ν =1050 - 1200. Distilled water (1000ml.) was added and the aqueous suspension was extracted with n-pentane (4x300ml.) The combined pentane extracts were washed with water (4x300ml.) and dried over magnesium sulphate. The volume of the solution was reduced in successive stages and each time cooled to 0° when a series of crops of pale yellow needles were obtained. Combinationwith the crystals previously obtained gave the total yield of α -phenyl - α (7-tropyl)acetaldehyde (53.0g,63%). A small portion was sublimed at room temperature.

M. Pt	80 - 81°
ν (Nujol mull)	3060(w), 3020(w), 2982(m), 2800(w)
	1710(s), 1601(w), 1492(m), 1402(m)
	1394(m), 752(s), 694(s).
λ_{max}(cyclohexane)	260 (3,400)
τ (CCl_4)	0.39 (doublet), J = 2.8c/s) IH,
	2.41 - 2.89 (complex multiplet) 5H,
	3.12 - 3.41 (complex multiplet) 2H,
	3.50 - 3.98 (complex multiplet) 2H,
	4.43 - 5.18 (complex multiplet) 2H,
	6.19 - (broad doublet, J = 11.5 c/s)IH,
	7.15 - 7.68 (complex multiplet) IH.
Analysis	Found: C, 86.0; H 6.8
	$C_{15}H_{14}O$ requires C, 85.7; H, 6.7%

α -Phenyl-α- (7-tropyl)acetaldehyde benzene sulphonyl hydrazone

α -phenyl-α- (7-tropyl)acetaldehyde (48.0g) and benzene sulphonyl hydrazide (40.0g) were added to methanol (800ml.) at room temperature and stirred vigorously. Theydissolved rapidly and almost immediately a flocculent white precipitate began to appear. After 30 minutes the reaction mixture was completely filled with precipitate. After one hour the reaction mixture was filtered and the white crystalline precipitate obtained washed with a little chilled methanol. Further product was obtained by adding portions of distilled water to the filtrate and cooling it to 0°. These crops were added to the initial product and dried under

vacuum over phosphorus pentoxide to give white granular crystals of α-phenyl - α- (7-tropyl) acetaldehyde benzene sulphonyl hydrazone (79.5.g., 96%)

M. Pt	147 - 149° (decomposes)
ν(Nujol mull)	322(s), 3085(w), 3063(w), 3020(m), 1604(w), 1586(m), 1497(m), 1482(w), 1401(m), 1346(m), 1323(s), 1264(vs), 1090(s), 1073(m), 1030(s), 1002(m), 954(m), 856(s), 847(s), 797(s).
U.V.	A featureless continuum leading to end absorption.
τ(CCl_4)	1.75 - 2.98 (overlapping complex multiplets) 11H, 3.18 - 3.42 (complex multiplet) 2H, 3.60 - 4.12 (complex multiplet)(2H, 4.85 - 5.28 (complex multiplet) 2H 6.22 (doublet of doublets, J = 11.8 c/s and 6.9 c/s) 1H, 7.60 - 8.18 (complex multiplet) 1H, 9.01 (singlet) 1H.
Analysis	Found: C,69.9; H,5.6; N, 7.6

$C_{21}H_{20}O_2N_2S$ requires C,69.2; H,5.55; N,7.7%

Preparation of the lithium salt of α-phenyl - α- (7-tropyl)acetaldehyde benzene sulphonyl hydrazone

α-phenyl-α-(7-tropyl)acetaldehyde benzene sulphonyl hydrazone (48.5g., 1mol.) was dissolved in dry tetrahydrofuran (800ml) and lithium methoxide (3.07g., 1 mol) added under an atmosphere of pure dry nitrogen. The tetrahydrofuran was removed under reduced pressure and the white crystalline product dried under vacuum over phosphorus pentoxide at room temperature. It was stored in a nitrogen dry box and used for pyrolysis as soon as possible. An I.R. spectrum(K.Br.disc) showed that the N-H stretching of the hydrazone (ν=3221) was absent.

Pyrolysis of α-phenyl - α- (7-tropyl) acetaldehyde benzene sulphonyl hydrazone (lithium salt).

The dry lithium salt, prepared as described previously was heated on an oil bath under high vacuum (0.05 - 0.1mm) and the products distilling collected in a trap, cooled by an acetone-dry ice mixture, which was placed as near as possible to the reaction flask. When the temperature of the bath reached 100° the lithium salt decomposed with effervescence and product began to distil. This collected in the cold trap giving an orange gum (3.5g.) which melted to give a viscous orange oil when allowed to warm to room temperature. An I.R. spectrum of the product indicated that it was essentially olefinic with traces of methanol and some other product, probably of a pyrazoline type. The product on T.L.C. (silica gel; light petroleum, methylene chloride 9:1) showed spots,

R_F: 0.516(w), 0.446(s), 0.321(w), 0.044(w), 0.0(s)

The use of methylene chloride as eluent showed that the spots R_F, 0.044 and 0.0 were composite and together included five or six compounds. V.P.C. (6ft., 20% ,ac column, oven temperature 190°) showed four major compounds and several minor ones. N.M.R. showed that the most abundant product had the spectrum reported for 9-phenylbicyclo (4,2,1) nonatriene.[104]

Separation of Reaction Mixture

The deep orange oil obtained was dissolved in the least possible amount of a mixture of light petroleum and methylene chloride (9:1), applied to a column of silica gel (200g.) and eluted withthe same solvent (1500ml.). The solvent was removed from the eluate to give a pale yellow oil (2.3g.). Both N.M.R. and I.R. indicated that the major component of this oil was 9-phenylbicyclo (4,2,1) nonatriene. The oil was dissolved in the least possible amount of a mixture of light petroleum and methylene chloride (9:1) and applied to a column of silica gel (400g.). Material was eluted with the same solvent in a cold room at 0°. The eluate was examined by U.V. spectroscopy for the presence of unsaturated compounds. The first 300 ml. of eluate contained no dissolved unsaturated compounds and was discarded; thereafter fractions of 100 ml. were collected. Fractions No.1-3 contained only traces of material as did fractions 16-20. Later fractions were completely blank. The u.v. spectra of the middle fractions showed complex changes which enabled a

rough division to be made which was examined more closely by N.M.R. and V.P.C. (6ft., 20% Lac column, oven temperature 190°). V.P.C. showed fractions 4,5 and 6 to be mainly (approx.80%) a single compound.

I.R.	Only Olefin bands.
u.v.	Broad featureless absorption
τ (CCl_4)	2.43 - 2.79 (complex multiplet) 5H,
	3.15 - 3.34 (complex multiplet) 2H,
	3.58 - 3.92 (complex multiplet) 2H,
	4.41 - 4.81 (complex) 4H,
	7.39 (broad triplet, J = 5.9c/s)1H.

The principal constituent of this mixture is believed to be 1-phenyl-1-(7-tropyl)ethylene.

Fractions No.9-14 all appeared to contain more than 90% of the desired 9-phenylbicyclo (4,2,1) nonatriene as indicated by V.P.C. and N.M.R. Fraction 12 crystallized to give colourless plates.

M.Pt	37 - 39°
Lit.value[112]	39 - 41°

Fractions 9 - 14 (932mg., 3.6%) were considered to be 9-phenylbicyclo (4,2,1)nonatriene. For kinetic measurements the compound was collected from a V.P.C. machine (Lac column, as previously) giving material of identical I.R., u.v., and N.M.R. to those reported.[104]

Bicyclo (4,2,1) nonatriene

Method of Cannell[107]

Norbornadiene was dimerized by heating it at 80° for two hours under an atmosphere of nitrogen in presence of a nickel carbonyl catalyst to give predominantly the endo-trans-exo dimer. This product was pyrolyzed by distilling it as slowly as possible through a tube packed with pyrex beads and heated to approximately 400° in a nitrogen atmosphere. The distillate was collected in a trap cooled by an acetone-dry ice mixture and cyclopentadiene removed by evaporation under reduced pressure to give bicyclo (4,2,1) nonatriene with properties identical to those reported.[107] V.P.C. (6ft., 20% Lac column, oven temperature 100°) showed that the product was at least 99% pure. This material was used for kinetic measurements without further purification.

SYNTHESIS OF BICYCLO(2.2.1)- COMPOUNDS

7-t-butoxynorbornadiene

Method of Story[108]

7-t-butoxynorbornadiene was prepared as described. Yield, 21% based on t-butyl perbenzoate (100g. scale). The product had properties identical to those described and in addition;

$\tau(CCl_4)$ 3.42 (multiplet) 2H, 3.52 (multiplet) 2H, 6.30 (broad singlet) 1H, 6.71 (multiplet) 2H, 8.93 (singlet) 9H

7-Phenylnorbornadiene

Modified method of Story and Fahrenholtz[109]

Freshly distilled phenyl bromide (31.2g., 0.2 moles) was dissolved in anhydrous ether (200ml.) and magnesium (4.8g.,0.2g. atom) added. The mixture was stirred until the reaction started and then cooled by ice-cold water to prevent the ether from boiling. When all the magnesium had dissolved methylcyclohexane was added in portions as the ether was removed by distillation. When the B.Pt of the mixture reached 95° the distillation was stopped and the reaction mixture allowed to cool to about 50°. 7-t-butoxynorbornadiene (16.4g., 0.1 mole) was added and the mixture stirred and heated under reflux. Aliquots were withdrawn at intervals and quenched by pouring into water, the aqueous mixture was extracted with n-pentane and the pentane extract washed with water and dried over magnesium sulphate. The pentane extract was reduced in bulk and the disappearance of the 7-t-butoxynorbornadiene followed by V.P.C. (6ft., 10% silicone gum rubber column; oven temperature 100°). Observation of the appearance of product required a higher oven temperature (130°). After 15 hours the 7-t-butoxynorbornadiene had completely disappeared and the reaction mixture was poured into water (300ml.) The aqueous mixture was extracted with n-pentane (4x100ml.) and the pentane extracts combined, washed with water, and dried over magnesium sulphate. The solvent was removed and the residue

fractionally distilled under reduced pressure. The fraction distilling at 60-61° / 0.1mm collected. 7-phenylnorbornadiene is reported to have B.Pt[109] 80-81° / 1.8mm.

Closer examination by V.P.C. (6ft. 5% carbowax column; oven temperature 160°) showed that the distilled fraction contained two compounds. N.M.R. showed only resonances in the aromatic region in addition to those reported for 7-phenylnorbornadiene.

The product was dissolved in n-pentane (100ml) and the pentane solution shaken vigorously for about a minute with an aqueous silver nitrate solution(100ml., 10% w/v). This was repeated four times. The aqueous silver nitrate extracts were combined and gaseous ammonia passed in until the brown precipitate initially formed had redissolved. The ammoniacal solution was cautiously extracted with n-pentane (5x50ml) and the combined pentane extracts washed with water and dried over magnesium sulphate. Removal of the solvent under reduced pressure gave 7-phenylnorbornadiene (6.2g., 0.0369 moles, 36.9%). The product was pure, as indicated by V.P.C. and had all physical properties as reported.[109]

7-Phenylnorbornane

7-phenylnorbornadiene (2.10g.) was dissolved in ethyl acetate (30 ml.) and 10% palladium on charcoal (240mg.) was added. Hydrogenation was carried out in the normal manner until 2 mols of hydrogen had been taken up (approx. 2 hours). The reaction mixture was filtered and the solvent removed under reduced pressure to give 7-phenylnorbornane (2.Rg., 98.5%)

The product appeared as a single peak under conditions which permitted the separation of starting material and product (6ft., 5% carbowax column, oven temperature 160°).

ν (liquid film)	3082(w), 3060(w), 3024(w)
	2955(s), 2916(w), 2870(m)
	1606(w), 1497(m), 1472(w)
	1453(w), 1348(w), 1311(w)
	1033(w), 882(w), 835(w)
	772(w), 723(s), 697(s).
λ_{max}(cyclohexane)	253 (206) 259 (237) 265 (181)

τ 2.70 (multiplet) 5H, 7.07 (broad singlet) 1H, 7.41 (multiplet) 2H 7.97 - 9.01 (complex) 8H

Analysis Found: C, 90.7; H, 9.25
$C_{13}H_{16}$ requires C, 90.6; H, 9.35%

7-Phenylnorbornene

After the method of Garbisch et al.[117]

7-phenylnorbornadiene (1.12g., 1 mol.), benzene sulphonyl hydrazide (0.86g., 1.5 mol.) and triethylamine (0.86g) were dissolved in diglyme (15ml.) The reaction mixture was heated on a water bath at 95°. Aliquots were removed at frequent intervals. They were poured into n-pentane; washed with dilute sulphuric acid, dilute sodium hydroxide, and water, then dried over magnesium sulphate. The n-pentane extracts were reduced to small bulk and examined by V.P.C. (6ft, 5% carbowax column, oven temperature 160°) under conditions which permitted the detection of two distinct products as they were formed. After 10 hours the reaction mixture was quenched by pouring into water and the hydrocarbon product extracted as from the aliquots previously. At this stage V.P.C. showed the reaction mixture to contain approximately 10% norbornadiene, 45% norbornene, and 45% norbornane. This product distribution was confirmed by an N.M.R. spectrum of the product mixture. This showed two peaks in the region corresponding to the vinyl proton resonances of a norbornene at 4.01 τ and 3.65 τ in the ratio

of at least 10:1. The reaction mixture was dissolved in a mixture of light petroleum and methylene chloride, 9:1, and applied to a column of silica gel (50g.). Products were eluted with the same solvent mixture and collected in 25ml. fractions. After removal of the solvent fractions 9 and 10 gave pure 7-phenylnorbornene (211mg., 19%).

ν (liquid film)	3044(w), 3011(w), 2960(s)
	2863(m), 1609(w), 1501(m)
	718(s), 691(s).
U.V.	A featureless shoulder leading to end absorption.
τ (CCl_4)	2.79 (multiplet)5H, 4.01(multiplet)
	2H, 6.84 (multiplet) 2H, 7.03 (multiplet) 1H,
	7.84 - 8.23 (complex multiplet) 2H,
	8.65 - 9.01 (complex multiplet) 2H.

KINETIC MEASUREMENTS

Base solutions

Solutions of potassium t-butoxide in perdeutero-dimethyl sulphoxide were made up in a nitrogen dry box from potassium t-butoxide which was stored in the dry box and perdeutero-dimethyl sulphoxide which was stood over molecular sieve type 4A in a dry box overnight before use. Solutions were 0.893M

(1.00g. potassium t-butoxide in 10.0 ml. perdeutero-dimethyl sulphoxide).

Standardization of Base Solutions

To 0.50 ml. of the base solution in a test tube in the dry box was added 0.050ml. cycloocta-1,5-diene. The test tube was stoppered with a serum cap and transferred to a water bath at 60 ± 0.1°. Aliquots of 0.10ml. were removed by syringe at intervals over a period of 30 minutes. They were quenched by addition to water and the aqueous mixture extracted with n-pentane. The proportion of cycloocta-1,5,-diene and cycloocta-1,3-diene in each extract was determined by V.P.C. (6ft. 20% Lac 446 column, oven temperature 80°).

Base solutions after kinetic runs were standardized by opening the N.M.R. tubes in the dry box, transferring the contents to a test tube and proceeding as previously.

Kinetic Measurements

Solutions for kinetic measurements consisted of 0.40 ml. 0.893 M potassium t-butoxide in perdeutero-dimethyl sulphoxide and 0.10 ml. of the appropriate hydrocarbon made up in a nitrogen dry box. Preliminary experiments were conducted in each case in N.M.R. tubes stoppered with small serum caps which were heated in a thermostatted bath and removed at intervals to have their

N.M.R. spectra recorded in a normal proton probe at 33.5°.

For the accurate kinetic runs quoted in the text the solutions were sealed in N.M.R. tubes under nitrogen and the spectra recorded using a Perkin Elmer Variable Temperature Probe set at the temperature stated.

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